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(71)Applicant : HOYA CORP

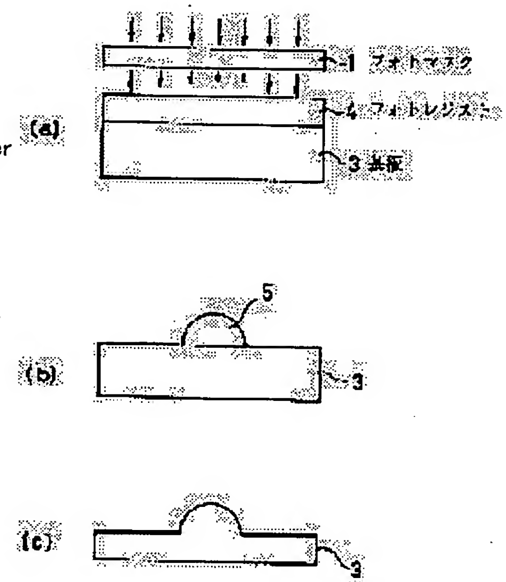
(72)Inventor : MIURA TOSHINOBU
MATSUMOTO KENJI
KOSUGE HIROYUKI
YAMAGUCHI YOICHI

(54) FORMATION OF THREE-DIMENSIONAL SHAPE, FORMED THREE-DIMENSIONAL STRUCTURE AND PRESS MOLD

(57)Abstract:

PURPOSE: To form a microscopically smooth three-dimensional surface shape and to provide a fine structure or a press mold.

CONSTITUTION: A resist 4 of which the ã-value is adjusted to 1.0 is applied to a substrate 3 to be exposed (a) by using a mask 1 having a specific shading pattern changing exosure intensity continuously. Subsequently, the resist 4 is developed by a developer to form a resist image 5 (b). Continuously, the resist image 5 is transferred to a substrate 3 to form a three-dimensional shape (object) (c).



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JAPANESE [JP,08-174563,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] The process which exposes said resist layer using the mask for lithography which has the protection-from-light nature pattern to which the exposure reinforcement which forms a resist layer on a base material and reaches this resist layer is changed continuously, The process which carries out the development of the resist layer after said exposure, and forms the resist image of a three-dimensions configuration, In the formation approach of a three-dimensions configuration of having the process which etches said resist image and base material into coincidence, and imprints the three-dimensions configuration of a resist image to a base material The formation approach of the three-dimensions configuration characterized by using the resist and/or the resist image formation conditions that the residual membrane curve of a resist turns into a residual membrane curve of a loose inclination.
[Claim 2] The formation approach of a three-dimensions configuration according to claim 1 that a resist which serves as a residual membrane curve of said loose inclination is a resist of low resolving power with low contrast.
[Claim 3] The formation approach of a three-dimensions configuration according to claim 1 or 2 that resist image formation conditions which serve as a residual membrane curve of said loose inclination are the baking conditions and/or the development conditions of a resist.
[Claim 4] The formation approach of claim 1 whose resist and/or resist image formation conditions which serve as a residual membrane curve of said loose inclination are conditions from which the contrast of a resist becomes 2.0 or less with a gamma value thru/or a three-dimensions configuration given in three.
[Claim 5] The formation approach of claim 1 characterized by performing reduced projection exposure in the process which exposes said resist layer thru/or a three-dimensions configuration given in four.
[Claim 6] The formation approach of claim 1 characterized by heating the resist image of this three-dimensions configuration at temperature higher than the melting point of this resist after the process which forms the resist image of a three-dimensions configuration by said development thru/or a three-dimensions configuration given in five.
[Claim 7] The three-dimensional structure object which was manufactured by the formation approach of claim 1 thru/or a three-dimensions configuration given in six and which sees microscopically and has the shape of smooth three-dimensions surface type.
[Claim 8] The press-forming mold which was manufactured by the formation approach of claim 1 thru/or a three-dimensions configuration given in six and which sees microscopically and has the shape of smooth three-dimensions surface type.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the formation approaches, such as a press-forming mold for mass-producing the microstructures which structure control was especially improved by precision to the three dimensions of a micro lens, a micro machine, a micro sensor, etc., and these microstructures about the formation approach of a three-dimensions configuration, etc.
[0002]
[Description of the Prior Art] In recent years, production of microstructures, such as a micro machine, is tried using the lithography technique used for semi-conductor manufacture etc. Although the method of applying a photoresist to the base material for microstructure formation, specifically exposing and developing [mind and] a photo mask, obtaining a resist pattern, imprinting this resist pattern to the base material for microstructure formation by etching, and manufacturing a microstructure is learned, if it is this approach, the configuration of the depth direction of the microstructure obtained is limited to the rectangle, and cannot control the configuration of the depth direction.
[0003] Then, various examination is carried out and the production approach of the microstructure which structure control was improved by precision is proposed by the three dimensions of a three-dimensions curved surface etc.
[0004] For example, heating fusion of the resin pattern array formed in the rectangle is carried out, it deforms into a spherical-surface configuration, and the approach of producing the convex type micro-lens array made of resin is proposed (it considers as a well-known example 1). (JP,5-40216,A)
[0005] Moreover, the approach of repeating exposure and development and producing a stair-like configuration as an option, is proposed (it considers as a well-known example 2). (journal vacuum Science technology, B9 (6), 1991, 3117 - 3120 pages)
[0006] Furthermore, the approach of producing the configuration according to the light exposure of an electron beam in changing the light exposure of an electron beam with an exposure location, exposing to an electron beam resist as other approaches, and developing this is proposed (it considers as a well-known example 3). (JP,2-44060,B)
[0007] Moreover, the light which made a part of spacing of the protection-from-light part of a photo mask below the diffraction limitation of exposure wavelength, and penetrated between this protection-from-light part exposes a photoresist through the photo mask which gives the amount of transmitted lights which changes continuously superficially. subsequently, by carrying out a development, the approach of forming the after-image resin pattern (resist image of a three-dimensions configuration) according to light exposure in the exposed field is proposed (eye I I [ ] — I proceedings-on em I em S — in 1994) 205 - 210 pages (it considers as a well-known example 4).
[0008] On the other hand, about the manufacture approach of the press-forming mold for mass-producing a microstructure, the approach of imprinting to a photopolymer the configuration of a transparence matrix where micro processing has been performed, and imprinting the imprinted photopolymer in the mold for substrate press molding by etching is proposed (it considers as a well-known example 5). (JP,6-15184,B)
[0009]
[Problem(s) to be Solved by the Invention] However, there is a problem as shown below in the production approach of the conventional microstructure mentioned above.
[0010] That is, if it is in the approach of well-known example 1 publication, there is a problem of keeping being restricted to what has the spherical configuration acquired since spherical-surface-ization is performed using the surface tension of the fused resin.
[0011] Moreover, if it is in the approach of well-known example 2 publication, since it is necessary to repeat processes, such as resist membrane formation, exposure, and development, two or more times, and to perform them, manufacture is complicated, and it is necessary to perform alignment of a photo mask and the exposed body strictly, and there is a problem that manufacture is difficult, technically.
[0012] Furthermore, if it is in the approach of well-known example 3 publication, since all patterns are drawn with the electron beam, exposure takes time amount and there is a problem that productivity is very low.
[0013] Moreover, if it is in the approach of well-known example 4 publication, the resist image of a three-dimensions configuration is producible with sufficient productivity, but since the shape of the surface type is stair-like (notched) when the resist image of a three-dimensions configuration actually producible by the approach of a well-known example 4 is seen microscopically, there is a problem that it is difficult to actually apply to manufacture of products, such as a micro lens as which the shape of smooth surface type is required.

[0014] Furthermore, if it is in the approach of well-known example 5 publication, since the matrix is produced by machining, producing the three-dimensions configuration of 100 micrometers or less has the problem of being difficult. In addition, if it is in production of the press die using a superhard ingredient, in order to usually perform grinding by the grinding stone, and polish, there is also a problem that the magnitude of a processed mold is restricted more than a millimeter.
[0015] This invention is made in view of the trouble mentioned above, and aims microscopic at offer of the formation approach of the shape of smooth three-dimensions surface type. Moreover, it aims at offer of the press-forming mold for mass-producing the microstructures which structure control was improved by precision, and these microstructures etc. to the three dimensions which have the shape of smooth three-dimensions surface type microscopically.
[0016]
[Means for Solving the Problem] In order to attain the above-mentioned purpose the formation approach of the three-dimensions configuration of this invention The process which exposes said resist layer using the mask for lithography which has the protection-from-light nature pattern to which the exposure reinforcement which forms a resist layer on a base material and reaches this resist layer is changed continuously, The process which carries out the development of the resist layer after said exposure, and forms the resist image of a three-dimensions configuration, In the formation approach of a three-dimensions configuration of having the process which etches said resist image and base material into coincidence, and imprints the three-dimensions configuration of a resist image to a base material The residual membrane curve of a resist is considered as the configuration which uses a resist and/or resist image formation conditions which serve as a residual membrane curve of a loose inclination.
[0017] Moreover, the formation approach of the three-dimensions configuration of this invention is set to the formation approach of the three-dimensions configuration of above-mentioned this invention. The configuration whose resist which serves as a residual membrane curve of said loose inclination is a resist of low resolving power with low contrast, The configuration whose resist image formation conditions which serve as a residual membrane curve of said loose inclination are the baking conditions and/or the development conditions of a resist, In the configuration whose resist and/or resist image formation conditions which serve as a residual membrane curve of said loose inclination are conditions from which the contrast of a resist becomes 2.0 or less with a gamma value, and the process which exposes said resist layer the configuration which performs reduced projection exposure — or — It has considered as the configuration which heats the resist image of this three-dimensions configuration at temperature higher than the melting point of this resist after the process which forms the resist image of a three-dimensions configuration by said development.
[0018] Moreover, the minute three-dimensional structure object of this invention is considered as the configuration which manufactures the three-dimensional structure object which sees microscopically and has the shape of smooth three-dimensions surface type by the formation approach of the above-mentioned three-dimensions configuration.
[0019] Furthermore, the press-forming mold of this invention is considered as the configuration which manufactures the press-forming mold which sees microscopically and has the shape of smooth three-dimensions surface type by the formation approach of the above-mentioned three-dimensions configuration.
[0020] Hereafter, this invention is explained to a detail. In the formation approach of the three-dimensions configuration of this invention, first, a resist layer is formed on a base material and said resist layer is exposed using the mask for lithography which has the protection-from-light nature pattern to which the exposure reinforcement which reaches this resist layer is changed continuously.
[0021] Here, although any ingredients can especially be used and it will not be restricted if it is the high ingredient of lightfastness or a mechanical strength as a base material ingredient, the engineering plastics represented by charges of an infrared-transparent material, such as glass ingredients, such as a superhard ingredient of SiC, WC, TiC, Cr3C2, TiN, and aluminum2O3 grade and a quartz, and Si, germanium, and polyamides are mentioned, for example. Although especially the configuration of a base material is not restricted, a substrate is usually used.
[0022] Moreover, formation of a resist layer is formed by the existing approaches, such as a spin coat, a DIP coat, and a spray coat, about a solution type resist, and is formed by the existing approaches, such as vacuum deposition, sputtering, and CVD, about solid type resists, such as an inorganic resist.
[0023] In this invention, the mask for lithography which has the protection-from-light nature pattern to which the exposure reinforcement which reaches a resist layer is changed continuously is used. Generally this is for changing continuously the exposure reinforcement to which it reaches a resist layer since the residual film thickness after the development of a resist changes corresponding to the exposure light reinforcement (light exposure) exposed on the resist, and changing the residual film thickness after the development of a resist continuously.
[0024] Here, some classes are mentioned as a mask for lithography which has the protection-from-light nature pattern to which the exposure reinforcement which reaches a resist layer is changed continuously. For example, the mask to which a part of optical density [at least] of a protection-from-light part was changed continuously is mentioned. Such a mask changes the thickness of a light-shielding film continuously, or changes the presentation of a light-shielding film continuously, and is obtained.
[0025] As other masks, the mask which made a part of spacing [at least] of the protection-from-light part of a mask spacing below the diffraction limitation of exposure wavelength, or the mask which made a part of spacing [at least] of the opening part of a mask spacing below the diffraction limitation of exposure wavelength is mentioned. In this case, what is necessary is just to carry out to below the marginal pitch that shows these spacing below, in

order to make spacing of the protection-from-light part of a mask, or spacing of an opening part into spacing below the diffraction limitation of exposure wavelength.

Pc=lambda/NA (1+sigma)

Here, in a marginal pitch and lambda, exposure wavelength and NA show the numerical aperture of an exposure machine, and sigma shows [Pc] the filling factor of the protection-from-light part in a pixel, respectively. Although the configuration of a protection-from-light part will not be restricted about the filling factor of a protection-from-light part here especially if it is a configuration which can carry out adjustable [of the face shield product in one pixel], configurations, such as the shape of the shape of a line and a dot and a rectangle, are mainly used.

[0026] In addition, if it is when carrying out contraction exposure using a stepper, spacing of the protection-from-light part of an actual mask (reticle) or spacing for opening is not made into spacing below the diffraction limitation of exposure wavelength, but it is made for spacing of a protection-from-light part or spacing for opening on the resist by which contraction projection was carried out to turn into spacing below the diffraction limitation of exposure wavelength.

[0027] When width of face (pitch) of the pattern which can be imprinted correctly, or area of a pattern is set to 1 and exposure reinforcement in this case is set to 1, without being influenced of diffraction, the mask mentioned above tends to make the width of face or area of a pattern one or less, and tends to obtain one or less in-between exposure reinforcement using the effect of diffraction.

[0028] As a mask of further others, the mask which made a part of spacing [at least] of the protection-from-light part of a mask spacing below the resolution limit of a resist, or the mask which made a part of spacing [at least] for opening of a mask spacing below the resolution limit of a resist is mentioned. For example, if the resolution limit of a resist is 1 micrometer, let spacing of the protection-from-light part of a mask, or spacing of an opening part be spacing of 1 micrometer or less. Since the marginal pitches mentioned above when the resolution limits (resolving power) of a resist differed also differ, this tends to take this into consideration. Therefore, if the resolution limit of a resist is 2 micrometers, let spacing of the protection-from-light part of a mask, or spacing of an opening part be spacing of 2 micrometers or less.

[0029] In addition, if it is a transparent ingredient to exposure wavelength as a mask substrate, all can use, and if it is the matter which can imprint the pattern which has the contrast of the optical density needed for a transferred object through a mask as a light-shielding film which constitutes the protection-from-light section, all can use about the formation ingredient of the mask for lithography which has the protection-from-light nature pattern to which the exposure reinforcement mentioned above is changed continuously. Specifically as a mask substrate, a quartz-glass plate, an aluminoborosilicate glass plate, etc. are mentioned, for example. Moreover, as a light-shielding film ingredient, chromium, chromic oxide, tungsten silicide, tantalum silicide, molybdenum silicide, silver colloid, etc. are mentioned, for example.

[0030] An electron ray mask besides a photo mask and an X-ray mask and an ion beam mask are also contained in the above-mentioned mask for lithography. Moreover, actual size exposure of adhesion exposure (contact exposure), contiguity exposure (pro squeak tee exposure), actual size projection exposure (mirror projection exposure), etc., reduced projection exposure, etc. are contained in the exposure approach. If reduced projection exposure is used, compared with actual size exposure, a more detailed microstructure can be formed easily. Furthermore, ultraviolet and the light, excimer laser, an X-ray (synchrotron radiation ****), an electron ray, an ion beam, etc. are contained in the exposure light source.

[0031] In this invention, in case the development of the resist layer after the above-mentioned exposure is carried out and the resist image of a three-dimensions configuration is formed, it is characterized by using the conditions in which the resist image which sees microscopically and has a smooth front face is formed. It is because it is stair-like if continuous change of this exposure reinforcement is seen microscopically although the exposure reinforcement which reaches a resist layer with the mask for lithography which has the above-mentioned specific protection-from-light nature pattern will change continuously, if contrast uses the resist of high resolving power with this high, so the front face of the resist image of the three-dimensions configuration acquired sees microscopically and becomes stair-like (notched).

[0032] Then, this invention persons invented using positively the conditions which cannot form a sharp resist image. Specifically by this invention, a resist and/or resist image formation conditions which serve as a residual membrane curve of a loose inclination are used.

[0033] Here, the residual membrane curve (characteristic curve) of a resist is a curve which takes the value (remaining rate of membrane) which took the common logarithm of an exposure along the axis of abscissa, and standardized the thickness after developing negatives on an axis of ordinate by spreading thickness, and is generally obtained, and the configurations (inclination etc.) of this residual membrane curve change with own properties (class of resin which constitutes a resist etc.) of a resist, the heat treatment conditions (prebaking conditions etc.) of a resist, development conditions, the exposure light sources, etc. Moreover, the inclination of a residual membrane curve is called a gamma value (gamma value), this gamma value serves as an index showing the contrast of a resist, and riser resolution also goes up contrast, so that this value is high. Generally, the gamma value of negative resist is defined by the inclination (tangent value of an angle of inclination) of a residual membrane curve in case a remaining rate of membrane is set to 0.5, and the gamma value of a positive resist is defined by the inclination of a residual membrane curve in case a remaining rate of membrane is set to 0.

[0034] Therefore, if a resist and resist image formation conditions which serve as a residual membrane curve of an inclination loose as a whole are used, the resist image of the smooth configurations (edge etc.) of low resolving

power where contrast is low can be formed. This is because the residual film thickness of a resist can be controlled in the range where exposure reinforcement is large as the inclination of a residual membrane curve is loose, and the resist residual film thickness according to a delicate change of exposure reinforcement can be obtained.
[0035] Here, although the resist of low resolving power with low contrast is mentioned as a resist which serves as a residual membrane curve of a loose inclination, such a resist carries out selection adjustment and prepares the content of the class of resin which constitutes a resist, a sensitization material, a solvent, etc., etc.
[0036] Moreover, as resist image formation conditions which serve as a residual membrane curve of a loose inclination, the baking conditions and/or the development conditions of a resist are mentioned. This is for the configuration of a residual membrane curve to change with the heat treatment conditions and development conditions of a resist, as mentioned above.
[0037] As development conditions, developing time, the development approach, the class of developer, concentration and temperature, the dissolution property of a resist, etc. are mentioned, and these conditions are set up so that it may become the residual membrane curve of a loose inclination. Since especially the dissolution property of developing time or a resist affects the resist configuration after development (resist profile), it sets up conditions in consideration of this. Since [which various these conditions are changed, actually creates a residual membrane curve specifically, and should just set up various conditions based on this] development temperature, the development approaches (spray ** in a spray method or convection-current rate of the developer in a dipping method), etc. affect resolution, conditions are set up in consideration of these again.
[0038] Prebaking is performed in order to usually remove a solvent out of the resist film, but in this invention, prebaking temperature and prebaking time amount are set up so that it may become the residual membrane curve of a loose inclination.
[0039] In addition, in the usual semi-conductor process, if a gamma value takes into consideration that the resist of 2.0 or more high contrast and high resolution is used, it can be said that they are the conditions from which the contrast of a resist becomes 2.0 or less with a gamma value as the resist and/or resist image formation conditions which serve as a residual membrane curve of a loose inclination. Here, like the case of the residual membrane curve mentioned above, since the value of a gamma value changes with the own property of a resist, the heat treatment conditions of a resist, development conditions, etc., if these are adjusted, it can acquire a desired gamma value. Although it is desirable that it is 2.0 or less from the above-mentioned reason as for the value of a gamma value, in order to make effectiveness of this invention into a clearer thing, it is desirable that a gamma value is 1.5 or less, and it is still more desirable that it is 1.0 or less. What is necessary is just to warn against becoming extremely low, since the resist residual film thickness according to a delicate change of exposure reinforcement is obtained about the minimum of a gamma value.
[0040] In addition, as a class of resin which constitutes a resist, photopolymerization nature resin, such as photodegradable resin, such as photocrosslinkable resins, such as a photodimerization mold photopolymer of a cinnamate system and a metal ion dichromic acid mold photopolymer, a photolysis bridge formation mold photopolymer of an azide system, a photolysis insoluble mold photopolymer of diazo **, and a photolysis meltable mold photopolymer of a quinone diazide system, an unsaturated polyester system photopolymer, an acrylate system photopolymer, a nylon system photopolymer, and a cationic polymerization system photopolymer, the inorganic resist of a chalcogenide type, etc. are mentioned, for example. These resin may be used independently, and may mix and use two or more kinds.
[0041] By this invention, the resist image of a three-dimensions configuration may be heated at temperature higher than the melting point of a resist after the process which forms the resist image of a three-dimensions configuration by the above-mentioned development. A resist deforms by this and it becomes smooth. Thus, if heating melting is performed after the above-mentioned process, compared with the case where heating fusion is carried out independently, the resist image of a three-dimensions configuration with them will be acquired for a short time. [there are few local defects with few waves, and smoother]
[0042] In this invention, after the above-mentioned development process, a resist image and a base material are etched into coincidence, and the three-dimensions configuration of a resist image is imprinted to a base material. In this case, for imprinting the same configuration as a resist image, the etch rate of a resist and a substrate base material is made equal. Moreover, for acquiring the configuration compressed into the lengthwise direction, the etch rate of a resist is made quicker than the etch rate of a substrate base material, and for acquiring the configuration conversely extended to the lengthwise direction, the etch rate of a resist is made later than the etch rate of a substrate base material.
[0043] In addition, since an etch rate changes with the etching conditions in the resist and etching system to be used, it needs to judge these synthetically and needs to choose etching conditions. Since an etch rate changes with conditions, such as structure (class) of equipment, an etching pressure (gas pressure), an etching output, a quantity of gas flow, and substrate temperature, in using a dry etching system especially, it is necessary to judge these synthetically and to choose etching conditions.
[0044] In addition, although wet etching and dry etching are mentioned as the etching approach, in order to imprint the configuration of a resist pattern to a substrate correctly as much as possible, it is desirable to adopt dry etching. Although especially a dry etching system is not restricted, well-known dry etching systems, such as parallel monotonous mold reactive-ion-etching equipment and magnetron ion etching equipment, are used, for example.
[0045] The mixed gas which contains the simple substance gas of CF4, CHF3, C2F6, a fluorine system that is represented by Cl2, and a chlorine system, or these gas as gas used for dry etching is desirable. Moreover, inert gas,

such as gas, such as oxygen or hydrogen, or helium, Ar, may be mixed in these gas if needed.
[0046] according to the above-mentioned this invention approach — microscopic — seeing — the shape of smooth three-dimensions surface type — it can form . Moreover, according to this invention approach, it is effective especially as the manufacture approach of the microoptics components which can manufacture efficiently the microstructure of the smooth front face which structure control was improved by precision to three dimensions, and need the shape of smooth surface type for them microscopically practically especially. Furthermore, according to this invention approach, the minute press-forming mold of the smooth front face which structure control was improved by precision to the three dimensions which were not able to be acquired conventionally can be manufactured efficiently. In addition, the formation approach of the three-dimensions configuration of this invention is not restricted to a microstructure, but can be applied also to the structure of the usual magnitude.
[0047] Other invention of this invention is three-dimensional structure objects characterized by manufacturing by the formation approach of the three-dimensions configuration mentioned above. The three-dimensional structure object of this invention is a microstructure which structure control was improved by precision to the three dimensions which have the shape of smooth three-dimensions surface type microscopically, and is effective especially as microoptics components which need the shape of smooth surface type microscopically practically. That is, conventionally, this invention attains utilization of the microoptics components which were not able to be obtained as a practical use product, and its utility value on industry is very high.
[0048] In addition, especially the application or class of microstructure are not restricted. As an application of a microstructure, the application as microoptics components, micro machine components, and micro sensor components is mentioned, for example. Moreover, as a class of microoptics components, gratings, such as spherical lenses and aspheric lenses, such as a convex type lens, a concave lens, an anamorphic lens, and a lenticular lens, a triangular waveform grating, a sinusoidal form grating, and a trapezoidal wave form grating, prism, a zone plate, a Fresnel lens, a holographic lens, etc. are mentioned. As a class of micro machine components or micro sensor components, a convex type spherical-surface object, a concave spherical-surface object, an aspheric surface object, a drill-like projection object, etc. are mentioned.
[0049] in addition, two or more microstructures [this invention] — arrangement of arbitration — arranging — being producible — producing a microstructure continuously further **** — the microstructure of continuation one apparatus — a continuum is producible.
[0050] Other invention of this invention is press-forming molds characterized by manufacturing by the formation approach of the three-dimensions configuration mentioned above. According to the press-forming mold of this invention, a microstructure can be mass-produced easily.
[0051] Here, although any ingredients can especially be used and it will not be restricted if it is lightfastness, thermal resistance, and the high ingredient of a mechanical strength as a base material processed into a minute press-forming mold, the engineering plastics represented by charges of an infrared-transparent material, such as glass ingredients, such as a superhard ingredient of SiC, WC, TiC, Cr3C2, TiN, and aluminum2O3 grade and a quartz, and Si, germanium, and polyamides are mentioned, for example.
[0052] In addition, glass, plastics, etc. are used as an ingredient to press. In this case, the optical glass of BK-7 grade is used as glass. Moreover, in using plastics as an ingredient to press, transparent materials, such as a quartz, are used for a press die, it is filled up with ultraviolet-rays hardening resin between a press die and a transferred substrate, ultraviolet rays are irradiated, resin is stiffened, and it can carry out press molding of the microoptics component made of resin etc. Here, as ultraviolet-rays hardening resin, well-known resin, such as mixture of polystyrene resin, an epoxy resin, urethane resin, polyolefin resin, polyimide resin, polyamide resin, polyester resin, or these resin, can be used.
[0053] Furthermore, a heat-resistant ingredient is used for a press die, and it is filled up with heat-curing resin between a press die and a transferred substrate, and with heating, heat-curing resin can be stiffened and the microoptics component made of resin etc. can also be cast. Here, as heat-curing resin, well-known resin, such as mixture of polystyrene resin, acrylic resin, an epoxy resin, urethane resin, polyolefin resin, polyimide resin, polyamide resin, polyester resin, or these resin, can be used.
[0054]
[Example] Hereafter, based on an example, this invention is explained still more concretely.
[0055] The positive type styrene system photoresist 4 corresponding to g line which adjusted the gamma value to 1.0 was applied on the example 1 quartz substrate 3, and the resist 4 was exposed with the actual size g line adhesion exposure machine using the photo mask 1 which has the circular protection-from-light pattern 2 as shown in drawing 1 (drawing 2 (a)). Here, what shall have the protection-from-light pattern 2 with which the occupancy area of a protection-from-light part decreases gradually toward a circle periphery, and spacing of a protection-from-light part made below the marginal pitch (Pc=0.11micrometer) was used for the photo mask 1 shown in drawing 1 .
[0056] Subsequently, the photoresist 4 was developed with the developer (AZ developer, by Hoechst A.G.) (developing time 120 seconds, prebaking temperature of 90 degrees C, time amount 60 minutes), and 20 micrometers of vertical angles and the convex type spherical-surface resist image 5 with a height of 1 micrometer were formed (drawing 2 (b)).
[0057] Using parallel monotonous mold reactive-ion-etching equipment, supply the high-frequency power of 250W and on then, C2F6 flow-rate 50sccm and the conditions which made the etch rate of a resist 4 the same as that of the etch rate of a substrate 3 Dry etching of the quartz substrate which has the above-mentioned convex type

spherical-surface resist image was carried out, the convex type spherical-surface resist image 5 was imprinted to the quartz substrate 3, and 20 micrometers of vertical angles and the convex type spherical-surface object made from a quartz with a height of 1 micrometer were formed (drawing 2 (c)).
[0058] 20 micrometers of vertical angles and the convex type spherical-surface object made from a quartz with a height of 1 micrometer which were acquired in the example 2 example 1 are made into a matrix, and it is filled up with a photopolymerization nature monomer (monomer INC312 for 2by Japanese chemistry medicine company P) between a matrix and a substrate. By the exposure reinforcement of 20 mW/cm2 The mercury-vapor lamp was irradiated for 240 seconds, polymerization hardening of the monomer was carried out, and 20 micrometers of vertical angles and the concave spherical-surface object made of resin with a depth of 1 micrometer were formed.
[0059] The positive type styrene system photoresist 4 corresponding to g line whose gamma value is 2.0 was applied on the example 3SiC substrate 3, and spacing of the protection-from-light part the part is indicated to be to drawing 3 exposed the resist 4 with the actual size g line adhesion exposure machine using the photo mask 1 (less than [Pc=0.11micrometer]) which has the protection-from-light pattern 2 which changes gradually (drawing 4 (a)).
[0060] Subsequently, the photoresist 4 was developed with the developer (AZ developer by Hoechst A.G.), further, heat treatment was performed for 30 minutes at 200 degrees C, and the sinusoidal diffraction-grating resist image 5 with a grid pitch 105.6micrometer and a grid depth of 0.698 micrometers was formed (drawing 4 (b)).
[0061] Then, using parallel monotonous mold reactive-ion-etching equipment, the high-frequency power of 250W was supplied, on CF4 flow-rate 40sccm and the conditions which made the etch rate of a resist 4 quicker than the etch rate of a substrate 3, dry etching of the SiC substrate which has the above-mentioned sinusoidal diffraction-grating resist image was carried out, the sinusoidal diffraction-grating resist image 5 was compressed and imprinted to the quartz substrate 3 in the lengthwise direction, and the sinusoidal diffraction grating with a grid pitch 105.6micrometer and a grid depth of 0.279 micrometers was formed (drawing 4 (c)).
[0062] The sinusoidal diffraction grating with a grid pitch 105.6micrometer obtained in the example 4 example 3 and a grid depth of 0.279 micrometers was made into the matrix, after heating the glass which consists of 70 % of the weight of silicon dioxides, 25 % of the weight of lead oxide, and some kinds of other trace element components, it pressed, and the glass sine wave diffraction grating with a grid pitch 105.6micrometer and a grid depth of 0.279 micrometers was formed.
[0063] The positive type styrene system photoresist 4 corresponding to g line which adjusted the gamma value to 0.7 was applied on the example 5SiC substrate 3, and the occupancy area of a protection-from-light part exposed the resist 4 using the photo mask 1 (less than [Pc=0.50micrometer]) which has the zona-orbicularis-like protection-from-light pattern 2 which decrease in number gradually toward the periphery the part is indicated to be to drawing 5 with 5 times many g line [as this] reduced-projection-exposure machine (drawing 6 (a)).
[0064] Subsequently, the photoresist 4 was developed with the developer (AZ developer by Hoechst A.G.), and the Fresnel lens resist image 5 by which the diameter of 48 micrometers and the configuration with a depth of 3.88 micrometers were reversed was formed (drawing 6 (b)).
[0065] Using parallel monotonous mold reactive-ion-etching equipment, supply the high-frequency power of 250W and on then, CF4 flow-rate 40sccm and the conditions which made the etch rate of a resist 4 quicker than the etch rate of a substrate 3 Carry out dry etching of the SiC substrate which has the Fresnel lens resist image by which the above-mentioned configuration was reversed, and the Fresnel lens resist image 5 by which the configuration was reversed is compressed and imprinted to the quartz substrate 3 in a lengthwise direction. The Fresnel lens object made from SiC with which the diameter of 48 micrometers and the configuration with a depth of 1.55 micrometers were reversed was formed (drawing 6 (c)).
[0066] After having made into the matrix the Fresnel lens object made from SiC with which the configuration acquired in the example 6 example 5 was reversed, being filled up with the epoxy resin which mixed and obtained Epicoat 152 by the oil-ized shell epoxy company, and the epicure 114 by the oil-ized shell epoxy company between the matrix and the quartz substrate and carrying out heat hardening for four days at 30 degrees C, the matrix was lengthened and removed and the Fresnel lens made of an epoxy resin with a diameter [of 48 micrometers] and a height of 1.55 micrometers was formed.
[0067] The positive type styrene system photoresist 4 corresponding to g line which adjusted the gamma value to 0.7 was applied on the example 7PMMA substrate 3, and the width of face of the protection-from-light part the part (it corresponds to the part of Illustration A) is indicated to be to drawing 7 exposed the resist 4 using the photo mask 1 (less than [Pc=0.50micrometer]) which has the protection-from-light pattern 2 which changes gradually with 5 times many g line [as this] reduced-projection-exposure machine (drawing 8 (a)).
[0068] Subsequently, the photoresist 4 was developed with the developer (AZ developer by Hoechst A.G.), and V ditch type resist image 5 with a slot include angle [of 120 degrees] and a channel depth of 40 micrometers was formed (drawing 8 (b)).
[0069] Using parallel monotonous mold reactive-ion-etching equipment, supply the high-frequency power of 250W and on then, CF4 flow-rate 40sccm and the conditions which made the etch rate of a resist 4 later than the etch rate of a substrate 3 Dry etching of the PMMA substrate which has the above-mentioned V ditch type resist image was carried out, V ditch type resist image 5 was extended and imprinted to the PMMA substrate 3 in the lengthwise direction, and V ditch type made from PMMA with a slot include angle [of 60 degrees] and a channel depth of 120 micrometers was formed (drawing 8 (c)).
[0070] In addition, when the front face of the microstructure formed in the above-mentioned examples 1-7 and a minute press-forming mold was observed by SEM (scanning electron microscope), it saw microscopically and having

the shape of smooth surface type was checked.

[0071] Although the desirable example was given above and this invention was explained, this invention is not necessarily limited to the above-mentioned example.

[0072]

[Effect of the Invention] As explained above, according to the formation approach of the shape of three-dimensions surface type of this invention, it sees microscopically and the shape of smooth three-dimensions surface type can be formed. Moreover, according to this invention approach, it is effective especially as the manufacture approach of the microoptics components which can manufacture efficiently the microstructure of the smooth front face which structure control was improved by precision to three dimensions, and need the shape of smooth surface type for them microscopically practically especially. Furthermore, according to this invention approach, the minute press-forming mold of the smooth front face which structure control was improved by precision to the three dimensions which were not able to be acquired conventionally can be manufactured efficiently.

[0073] Moreover, the minute three-dimensional structure object which sees microscopically [this invention] and has the shape of smooth three-dimensions surface type attains utilization of the microoptics components which were not able to be conventionally obtained as a practical use product, and is very high. [of the utility value on industry]

[0074] Furthermore, according to the press-forming mold of this invention, a microstructure can be mass-produced easily.

[Translation done.]

TECHNICAL FIELD

[Industrial Application] This invention relates to the formation approaches, such as a press-forming mold for mass-producing the microstructures which structure control was especially improved by precision to the three dimensions of a micro lens, a micro machine, a micro sensor, etc., and these microstructures about the formation approach of a three-dimensions configuration, etc.

[Translation done.]

PRIOR ART

[Description of the Prior Art] In recent years, production of microstructures, such as a micro machine, is tried using the lithography technique used for semi-conductor manufacture etc. Although the method of applying a photoresist to the base material for microstructure formation, specifically exposing and developing [mind and] a photo mask, obtaining a resist pattern, imprinting this resist pattern to the base material for microstructure formation by etching, and manufacturing a microstructure is learned, if it is this approach, the configuration of the depth direction of the microstructure obtained is limited to the rectangle, and cannot control the configuration of the depth direction.
[0003] Then, various examination is carried out and the production approach of the microstructure which structure control was improved by precision is proposed by the three dimensions of a three-dimensions curved surface etc.
[0004] For example, heating fusion of the resin pattern array formed in the rectangle is carried out, it deforms into a spherical-surface configuration, and the approach of producing the convex type micro-lens array made of resin is proposed (it considers as a well-known example 1). (JP,5-40216,A)
[0005] Moreover, the approach of repeating exposure and development and producing a stair-like configuration as an option, is proposed (it considers as a well-known example 2). (journal vacuum Science technology, B9 (6), 1991, 3117 - 3120 pages)
[0006] Furthermore, the approach of producing the configuration according to the light exposure of an electron beam in changing the light exposure of an electron beam with an exposure location, exposing to an electron beam resist as other approaches, and developing this is proposed (it considers as a well-known example 3). (JP,2-44060,B)
[0007] Moreover, let the photo mask which gives the amount of transmitted lights from which the light which made a part of spacing of the protection-from-light part of a photo mask below the diffraction limitation of exposure wavelength, and penetrated between this protection-from-light part changes continuously superficially pass. The approach of forming the after-image resin pattern (resist image of a three-dimensions configuration) according to light exposure in the exposed field is proposed by exposing a photoresist and subsequently carrying out a development (it considers as a well-known example 4). (eye I I I proceedings-on em I em S, 1994, 205 - 210 pages)
[0008] On the other hand, about the manufacture approach of the press-forming mold for mass-producing a microstructure, the approach of imprinting to a photopolymer the configuration of a transparence matrix where micro processing has been performed, and imprinting the imprinted photopolymer in the mold for substrate press molding by etching is proposed (it considers as a well-known example 5). (JP,6-15184,B)

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, according to the formation approach of the shape of three-dimensions surface type of this invention, it sees microscopically and the shape of smooth three-dimensions surface type can be formed. Moreover, according to this invention approach, it is effective especially as the manufacture approach of the microoptics components which can manufacture efficiently the microstructure of the smooth front face which structure control was improved by precision to three dimensions, and need the shape of smooth surface type for them microscopically practically especially. Furthermore, according to this invention approach, the minute press-forming mold of the smooth front face which structure control was improved by precision to the three dimensions which were not able to be acquired conventionally can be manufactured efficiently.
[0073] Moreover, the minute three-dimensional structure object which sees microscopically [this invention] and has the shape of smooth three-dimensions surface type attains utilization of the microoptics components which were not able to be conventionally obtained as a practical use product, and is very high. [of the utility value on industry]
[0074] Furthermore, according to the press-forming mold of this invention, a microstructure can be mass-produced easily.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, there is a problem as shown below in the production approach of the conventional microstructure mentioned above.
[0010] That is, if it is in the approach of well-known example 1 publication, there is a problem of keeping being restricted to what has the spherical configuration acquired since spherical-surface-ization is performed using the surface tension of the fused resin.
[0011] Moreover, if it is in the approach of well-known example 2 publication, since it is necessary to repeat processes, such as resist membrane formation, exposure, and development, two or more times, and to perform them, manufacture is complicated, and it is necessary to perform alignment of a photo mask and the exposed body strictly, and there is a problem that manufacture is difficult, technically.
[0012] Furthermore, if it is in the approach of well-known example 3 publication, since all patterns are drawn with the electron beam, exposure takes time amount and there is a problem that productivity is very low.
[0013] Moreover, if it is in the approach of well-known example 4 publication, the resist image of a three-dimensions configuration is producible with sufficient productivity, but since the shape of the surface type is stair-like (notched) when the resist image of a three-dimensions configuration actually producible by the approach of a well-known example 4 is seen microscopically, there is a problem that it is difficult to actually apply to manufacture of products, such as a micro lens as which the shape of smooth surface type is required.
[0014] Furthermore, if it is in the approach of well-known example 5 publication, since the matrix is produced by machining, producing the three-dimensions configuration of 100 micrometers or less has the problem of being difficult. In addition, if it is in production of the press die using a superhard ingredient, in order to usually perform grinding by the grinding stone, and polish, there is also a problem that the magnitude of a processed mold is restricted more than a millimeter.
[0015] This invention is made in view of the trouble mentioned above, and aims microscopic at offer of the formation approach of the shape of smooth three-dimensions surface type. Moreover, it aims at offer of the press-forming mold for mass-producing the microstructures which structure control was improved by precision, and these microstructures etc. to the three dimensions which have the shape of smooth three-dimensions surface type microscopically.

[Translation done.]

MEANS

[Means for Solving the Problem] In order to attain the above-mentioned purpose the formation approach of the three-dimensions configuration of this invention The process which exposes said resist layer using the mask for lithography which has the protection-from-light nature pattern to which the exposure reinforcement which forms a resist layer on a base material and reaches this resist layer is changed continuously, The process which carries out the development of the resist layer after said exposure, and forms the resist image of a three-dimensions configuration, In the formation approach of a three-dimensions configuration of having the process which etches said resist image and base material into coincidence, and imprints the three-dimensions configuration of a resist image to a base material The residual membrane curve of a resist is considered as the configuration which uses a resist and/or resist image formation conditions which serve as a residual membrane curve of a loose inclination.
[0017] Moreover, the formation approach of the three-dimensions configuration of this invention is set to the formation approach of the three-dimensions configuration of above-mentioned this invention. The configuration whose resist which serves as a residual membrane curve of said loose inclination is a resist of low resolving power with low contrast, The configuration whose resist image formation conditions which serve as a residual membrane curve of said loose inclination are the baking conditions and/or the development conditions of a resist, In the configuration whose resist and/or resist image formation conditions which serve as a residual membrane curve of said loose inclination are conditions from which the contrast of a resist becomes 2.0 or less with a gamma value, and the process which exposes said resist layer the configuration which performs reduced projection exposure — or — It has considered as the configuration which heats the resist image of this three-dimensions configuration at temperature higher than the melting point of this resist after the process which forms the resist image of a three-dimensions configuration by said development.
[0018] Moreover, the minute three-dimensional structure object of this invention is considered as the configuration which manufactures the three-dimensional structure object which sees microscopically and has the shape of smooth three-dimensions surface type by the formation approach of the above-mentioned three-dimensions configuration.
[0019] Furthermore, the press-forming mold of this invention is considered as the configuration which manufactures the press-forming mold which sees microscopically and has the shape of smooth three-dimensions surface type by the formation approach of the above-mentioned three-dimensions configuration.
[0020] Hereafter, this invention is explained to a detail. In the formation approach of the three-dimensions configuration of this invention, first, a resist layer is formed on a base material and said resist layer is exposed using the mask for lithography which has the protection-from-light nature pattern to which the exposure reinforcement which reaches this resist layer is changed continuously.
[0021] Here, although any ingredients can especially be used and it will not be restricted if it is the high ingredient of lightfastness or a mechanical strength as a base material ingredient, the engineering plastics represented by charges of an infrared-transparent material, such as glass ingredients, such as a superhard ingredient of SiC, WC, TiC, Cr3C2, TiN, and aluminum2O3 grade and a quartz, and Si, germanium, and polyamides are mentioned, for example. Although especially the configuration of a base material is not restricted, a substrate is usually used.
[0022] Moreover, formation of a resist layer is formed by the existing approaches, such as a spin coat, a DIP coat, and a spray coat, about a solution type resist, and is formed by the existing approaches, such as vacuum deposition, sputtering, and CVD, about solid type resists, such as an inorganic resist.
[0023] In this invention, the mask for lithography which has the protection-from-light nature pattern to which the exposure reinforcement which reaches a resist layer is changed continuously is used. Generally this is for changing continuously the exposure reinforcement to which it reaches a resist layer since the residual film thickness after the development of a resist changes corresponding to the exposure light reinforcement (light exposure) exposed on the resist, and changing the residual film thickness after the development of a resist continuously.
[0024] Here, some classes are mentioned as a mask for lithography which has the protection-from-light nature pattern to which the exposure reinforcement which reaches a resist layer is changed continuously. For example, the mask to which a part of optical density [at least] of a protection-from-light part was changed continuously is mentioned. Such a mask changes the thickness of a light-shielding film continuously, or changes the presentation of a light-shielding film continuously, and is obtained.
[0025] As other masks, the mask which made a part of spacing [at least] of the protection-from-light part of a mask spacing below the diffraction limitation of exposure wavelength, or the mask which made a part of spacing [at least] of the opening part of a mask spacing below the diffraction limitation of exposure wavelength is mentioned. In

this case, what is necessary is just to carry out to below the marginal pitch that shows these spacing below, in order to make spacing of the protection-from-light part of a mask, or spacing of an opening part into spacing below the diffraction limitation of exposure wavelength.

Pc=lambda/NA (1+sigma)

Here, in a marginal pitch and lambda, exposure wavelength and NA show the numerical aperture of an exposure machine, and sigma shows [Pc] the filling factor of the protection-from-light part in a pixel, respectively. Although the configuration of a protection-from-light part will not be restricted about the filling factor of a protection-from-light part here especially if it is a configuration which can carry out adjustable [of the face shield product in one pixel], configurations, such as the shape of the shape of a line and a dot and a rectangle, are mainly used.

[0026] In addition, if it is when carrying out contraction exposure using a stepper, spacing of the protection-from-light part of an actual mask (reticle) or spacing for opening is not made into spacing below the diffraction limitation of exposure wavelength, but it is made for spacing of a protection-from-light part or spacing for opening on the resist by which contraction projection was carried out to turn into spacing below the diffraction limitation of exposure wavelength.

[0027] When width of face (pitch) of the pattern which can be imprinted correctly, or area of a pattern is set to 1 and exposure reinforcement in this case is set to 1, without being influenced of diffraction, the mask mentioned above tends to make the width of face or area of a pattern one or less, and tends to obtain one or less in-between exposure reinforcement using the effect of diffraction.

[0028] As a mask of further others, the mask which made a part of spacing [at least] of the protection-from-light part of a mask spacing below the resolution limit of a resist, or the mask which made a part of spacing [at least] for opening of a mask spacing below the resolution limit of a resist is mentioned. For example, if the resolution limit of a resist is 1 micrometer, let spacing of the protection-from-light part of a mask, or spacing of an opening part be spacing of 1 micrometer or less. Since the marginal pitches mentioned above when the resolution limits (resolving power) of a resist differed also differ, this tends to take this into consideration. Therefore, if the resolution limit of a resist is 2 micrometers, let spacing of the protection-from-light part of a mask, or spacing of an opening part be spacing of 2 micrometers or less.

[0029] In addition, if it is a transparent ingredient to exposure wavelength as a mask substrate, all can use, and if it is the matter which can imprint the pattern which has the contrast of the optical density needed for a transferred object through a mask as a light-shielding film which constitutes the protection-from-light section, all can use about the formation ingredient of the mask for lithography which has the protection-from-light nature pattern to which the exposure reinforcement mentioned above is changed continuously. Specifically as a mask substrate, a quartz-glass plate, an aluminoborosilicate glass plate, etc. are mentioned, for example. Moreover, as a light-shielding film ingredient, chromium, chromic oxide, tungsten silicide, tantalum silicide, molybdenum silicide, silver colloid, etc. are mentioned, for example.

[0030] An electron ray mask besides a photo mask and an X-ray mask and an ion beam mask are also contained in the above-mentioned mask for lithography. Moreover, actual size exposure of adhesion exposure (contact exposure), contiguity exposure (pro squeak tee exposure), actual size projection exposure (mirror projection exposure), etc., reduced projection exposure, etc. are contained in the exposure approach. If reduced projection exposure is used, compared with actual size exposure, a more detailed microstructure can be formed easily. Furthermore, ultraviolet and the light, excimer laser, an X-ray (synchrotron radiation ****), an electron ray, an ion beam, etc. are contained in the exposure light source.

[0031] In this invention, in case the development of the resist layer after the above-mentioned exposure is carried out and the resist image of a three-dimensions configuration is formed, it is characterized by using the conditions in which the resist image which sees microscopically and has a smooth front face is formed. It is because it is stair-like if continuous change of this exposure reinforcement is seen microscopically although the exposure reinforcement which reaches a resist layer with the mask for lithography which has the above-mentioned specific protection-from-light nature pattern will change continuously, if contrast uses the resist of high resolving power with this high, so the front face of the resist image of the three-dimensions configuration acquired sees microscopically and becomes stair-like (notched).

[0032] Then, this invention persons invented using positively the conditions which cannot form a sharp resist image. Specifically by this invention, a resist and/or resist image formation conditions which serve as a residual membrane curve of a loose inclination are used.

[0033] Here, the residual membrane curve (characteristic curve) of a resist is a curve which takes the value (remaining rate of membrane) which took the common logarithm of an exposure along the axis of abscissa, and standardized the thickness after developing negatives on an axis of ordinate by spreading thickness, and is generally obtained, and the configurations (inclination etc.) of this residual membrane curve change with own properties (class of resin which constitutes a resist etc.) of a resist, the heat treatment conditions (prebaking conditions etc.) of a resist, development conditions, the exposure light sources, etc. Moreover, the inclination of a residual membrane curve is called a gamma value (gamma value), this gamma value serves as an index showing the contrast of a resist, and riser resolution also goes up contrast, so that this value is high. Generally, the gamma value of negative resist is defined by the inclination (tangent value of an angle of inclination) of a residual membrane curve in case a remaining rate of membrane is set to 0.5, and the gamma value of a positive resist is defined by the inclination of a residual membrane curve in case a remaining rate of membrane is set to 0.

[0034] Therefore, if a resist and resist image formation conditions which serve as a residual membrane curve of an

inclination loose as a whole are used, the resist image of the smooth configurations (edge etc.) of low resolving power where contrast is low can be formed. This is because the residual film thickness of a resist can be controlled in the range where exposure reinforcement is large as the inclination of a residual membrane curve is loose, and the resist residual film thickness according to a delicate change of exposure reinforcement can be obtained.

[0035] Here, although the resist of low resolving power with low contrast is mentioned as a resist which serves as a residual membrane curve of a loose inclination, such a resist carries out selection adjustment and prepares the content of the class of resin which constitutes a resist, a sensitization material, a solvent, etc., etc.

[0036] Moreover, as resist image formation conditions which serve as a residual membrane curve of a loose inclination, the baking conditions and/or the development conditions of a resist are mentioned. This is for the configuration of a residual membrane curve to change with the heat treatment conditions and development conditions of a resist, as mentioned above.

[0037] As development conditions, developing time, the development approach, the class of developer, concentration and temperature, the dissolution property of a resist, etc. are mentioned, and these conditions are set up so that it may become the residual membrane curve of a loose inclination. Since especially the dissolution property of developing time or a resist affects the resist configuration after development (resist profile), it sets up conditions in consideration of this. Since [which various these conditions are changed, actually creates a residual membrane curve specifically, and should just set up various conditions based on this] development temperature, the development approaches (spray ** in a spray method or convection-current rate of the developer in a dipping method), etc. affect resolution, conditions are set up in consideration of these again.

[0038] Prebaking is performed in order to usually remove a solvent out of the resist film, but in this invention, prebaking temperature and prebaking time amount are set up so that it may become the residual membrane curve of a loose inclination.

[0039] In addition, in the usual semi-conductor process, if a gamma value takes into consideration that the resist of 2.0 or more high contrast and high resolution is used, it can be said that they are the conditions from which the contrast of a resist becomes 2.0 or less with a gamma value as the resist and/or resist image formation conditions which serve as a residual membrane curve of a loose inclination. Here, like the case of the residual membrane curve mentioned above, since the value of a gamma value changes with the own property of a resist, the heat treatment conditions of a resist, development conditions, etc., if these are adjusted, it can acquire a desired gamma value. Although it is desirable that it is 2.0 or less from the above-mentioned reason as for the value of a gamma value, in order to make effectiveness of this invention into a clearer thing, it is desirable that a gamma value is 1.5 or less, and it is still more desirable that it is 1.0 or less. What is necessary is just to warn against becoming extremely low, since the resist residual film thickness according to a delicate change of exposure reinforcement is obtained about the minimum of a gamma value.

[0040] In addition, as a class of resin which constitutes a resist, photopolymerization nature resin, such as photodegradable resin, such as photocrosslinkable resins, such as a photodimerization mold photopolymer of a cinnamate system and a metal ion dichromic acid mold photopolymer, a photolysis bridge formation mold photopolymer of an azide system, a photolysis insoluble mold photopolymer of diazo **, and a photolysis meltable mold photopolymer of a quinone diazide system, an unsaturated polyester system photopolymer, an acrylate system photopolymer, a nylon system photopolymer, and a cationic polymerization system photopolymer, the inorganic resist of a chalcogenide type, etc. are mentioned, for example. These resin may be used independently, and may mix and use two or more kinds.

[0041] By this invention, the resist image of a three-dimensions configuration may be heated at temperature higher than the melting point of a resist after the process which forms the resist image of a three-dimensions configuration by the above-mentioned development. A resist deforms by this and it becomes smooth. Thus, if heating melting is performed after the above-mentioned process, compared with the case where heating fusion is carried out independently, the resist image of a three-dimensions configuration with them will be acquired for a short time. [there are few local defects with few waves, and smoother]

[0042] In this invention, after the above-mentioned development process, a resist image and a base material are etched into coincidence, and the three-dimensions configuration of a resist image is imprinted to a base material. In this case, for imprinting the same configuration as a resist image, the etch rate of a resist and a substrate base material is made equal. Moreover, for acquiring the configuration compressed into the lengthwise direction, the etch rate of a resist is made quicker than the etch rate of a substrate base material, and for acquiring the configuration conversely extended to the lengthwise direction, the etch rate of a resist is made later than the etch rate of a substrate base material.

[0043] In addition, since an etch rate changes with the etching conditions in the resist and etching system to be used, it needs to judge these synthetically and needs to choose etching conditions. Since an etch rate changes with conditions, such as structure (class) of equipment, an etching pressure (gas pressure), an etching output, a quantity of gas flow, and substrate temperature, in using a dry etching system especially, it is necessary to judge these synthetically and to choose etching conditions.

[0044] In addition, although wet etching and dry etching are mentioned as the etching approach, in order to imprint the configuration of a resist pattern to a substrate correctly as much as possible, it is desirable to adopt dry etching. Although especially a dry etching system is not restricted, well-known dry etching systems, such as parallel monotonous mold reactive-ion-etching equipment and magnetron ion etching equipment, are used, for example.

[0045] The mixed gas which contains the simple substance gas of CF4, CHF3, C2F6, a fluorine system that is

represented by Cl2, and a chlorine system, or these gas as gas used for dry etching is desirable. Moreover, inert gas, such as gas, such as oxygen or hydrogen, or helium, Ar, may be mixed in these gas if needed.
[0046] according to the above-mentioned this invention approach — microscopic — seeing — the shape of smooth three-dimensions surface type — it can form . Moreover, according to this invention approach, it is effective especially as the manufacture approach of the microoptics components which can manufacture efficiently the microstructure of the smooth front face which structure control was improved by precision to three dimensions, and need the shape of smooth surface type for them microscopically practically especially. Furthermore, according to this invention approach, the minute press-forming mold of the smooth front face which structure control was improved by precision to the three dimensions which were not able to be acquired conventionally can be manufactured efficiently. In addition, the formation approach of the three-dimensions configuration of this invention is not restricted to a microstructure, but can be applied also to the structure of the usual magnitude.
[0047] Other invention of this invention is three-dimensional structure objects characterized by manufacturing by the formation approach of the three-dimensions configuration mentioned above. The three-dimensional structure object of this invention is a microstructure which structure control was improved by precision to the three dimensions which have the shape of smooth three-dimensions surface type microscopically, and is effective especially as microoptics components which need the shape of smooth surface type microscopically practically. That is, conventionally, this invention attains utilization of the microoptics components which were not able to be obtained as a practical use product, and its utility value on industry is very high.
[0048] In addition, especially the application or class of microstructure are not restricted. As an application of a microstructure, the application as microoptics components, micro machine components, and micro sensor components is mentioned, for example. Moreover, as a class of microoptics components, gratings, such as spherical lenses and aspheric lenses, such as a convex type lens, a concave lens, an anamorphic lens, and a lenticular lens, a triangular waveform grating, a sinusoidal form grating, and a trapezoidal wave form grating, prism, a zone plate, a Fresnel lens, a holographic lens, etc. are mentioned. As a class of micro machine components or micro sensor components, a convex type spherical-surface object, a concave spherical-surface object, an aspheric surface object, a drill-like projection object, etc. are mentioned.
[0049] in addition, two or more microstructures [this invention] — arrangement of arbitration — arranging — being producible — producing a microstructure continuously further **** — the microstructure of continuation one apparatus — a continuum is producible.
[0050] Other invention of this invention is press-forming molds characterized by manufacturing by the formation approach of the three-dimensions configuration mentioned above. According to the press-forming mold of this invention, a microstructure can be mass-produced easily.
[0051] Here, although any ingredients can especially be used and it will not be restricted if it is lightfastness, thermal resistance, and the high ingredient of a mechanical strength as a base material processed into a minute press-forming mold, the engineering plastics represented by charges of an infrared-transparent material, such as glass ingredients, such as a superhard ingredient of SiC, WC, TiC, Cr3C2, TiN, and aluminum2O3 grade and a quartz, and Si, germanium, and polyamides are mentioned, for example.
[0052] In addition, glass, plastics, etc. are used as an ingredient to press. In this case, the optical glass of BK-7 grade is used as glass. Moreover, in using plastics as an ingredient to press, transparent materials, such as a quartz, are used for a press die, it is filled up with ultraviolet-rays hardening resin between a press die and a transferred substrate, ultraviolet rays are irradiated, resin is stiffened, and it can carry out press molding of the microoptics component made of resin etc. Here, as ultraviolet-rays hardening resin, well-known resin, such as mixture of polystyrene resin, an epoxy resin, urethane resin, polyolefin resin, polyimide resin, polyamide resin, polyester resin, or these resin, can be used.
[0053] Furthermore, a heat-resistant ingredient is used for a press die, and it is filled up with heat-curing resin between a press die and a transferred substrate, and with heating, heat-curing resin can be stiffened and the microoptics component made of resin etc. can also be cast. Here, as heat-curing resin, well-known resin, such as mixture of polystyrene resin, acrylic resin, an epoxy resin, urethane resin, polyolefin resin, polyimide resin, polyamide resin, polyester resin, or these resin, can be used.

[Translation done.]

EXAMPLE

[Example] Hereafter, based on an example, this invention is explained still more concretely.
[0055] The positive type styrene system photoresist 4 corresponding to g line which adjusted the gamma value to 1.0 was applied on the example 1 quartz substrate 3, and the resist 4 was exposed with the actual size g line adhesion exposure machine using the photo mask 1 which has the circular protection-from-light pattern 2 as shown in drawing 1 (drawing 2 (a)). Here, what shall have the protection-from-light pattern 2 with which the occupancy area of a protection-from-light part decreases gradually toward a circle periphery, and spacing of a protection-from-light part made below the marginal pitch (Pc=0.11micrometer) was used for the photo mask 1 shown in drawing 1 .
[0056] Subsequently, the photoresist 4 was developed with the developer (AZ developer by Hoechst A.G.) (developing time 120 seconds, prebaking temperature of 90 degrees C, time amount 60 minutes), and 20 micrometers of vertical angles and the convex type spherical-surface resist image 5 with a height of 1 micrometer were formed (drawing 2 (b)).
[0057] Using parallel monotonous mold reactive-ion-etching equipment, supply the high-frequency power of 250W and on then, C2F6 flow-rate 50sccm and the conditions which made the etch rate of a resist 4 the same as that of the etch rate of a substrate 3 Dry etching of the quartz substrate which has the above-mentioned convex type spherical-surface resist image was carried out, the convex type spherical-surface resist image 5 was imprinted to the quartz substrate 3, and 20 micrometers of vertical angles and the convex type spherical-surface object made from a quartz with a height of 1 micrometer were formed (drawing 2 (c)).
[0058] 20 micrometers of vertical angles and the convex type spherical-surface object made from a quartz with a height of 1 micrometer which were acquired in the example 2 example 1 are made into a matrix, and it is filled up with a photopolymerization nature monomer (monomer INC312 for 2by Japanese chemistry medicine company P) between a matrix and a substrate. By the exposure reinforcement of 20 mW/cm2 The mercury-vapor lamp was irradiated for 240 seconds, polymerization hardening of the monomer was carried out, and 20 micrometers of vertical angles and the concave spherical-surface object made of resin with a depth of 1 micrometer were formed.
[0059] The positive type styrene system photoresist 4 corresponding to g line whose gamma value is 2.0 was applied on the example 3SiC substrate 3, and spacing of the protection-from-light part the part is indicated to be to drawing 3 exposed the resist 4 with the actual size g line adhesion exposure machine using the photo mask 1 (less than [Pc=0.11micrometer]) which has the protection-from-light pattern 2 which changes gradually (drawing 4 (a)).
[0060] Subsequently, the photoresist 4 was developed with the developer (AZ developer by Hoechst A.G.), further, heat treatment was performed for 30 minutes at 200 degrees C, and the sinusoidal diffraction-grating resist image 5 with a grid pitch 105.6micrometer and a grid depth of 0.698 micrometers was formed (drawing 4 (b)).
[0061] Then, using parallel monotonous mold reactive-ion-etching equipment, the high-frequency power of 250W was supplied, on CF4 flow-rate 40sccm and the conditions which made the etch rate of a resist 4 quicker than the etch rate of a substrate 3, dry etching of the SiC substrate which has the above-mentioned sinusoidal diffraction-grating resist image was carried out, the sinusoidal diffraction-grating resist image 5 was compressed and imprinted to the quartz substrate 3 in the lengthwise direction, and the sinusoidal diffraction grating with a grid pitch 105.6micrometer and a grid depth of 0.279 micrometers was formed (drawing 4 (c)).
[0062] The sinusoidal diffraction grating with a grid pitch 105.6micrometer obtained in the example 4 example 3 and a grid depth of 0.279 micrometers was made into the matrix, after heating the glass which consists of 70 % of the weight of silicon dioxides, 25 % of the weight of lead oxide, and some kinds of other trace element components, it pressed, and the glass sine wave diffraction grating with a grid pitch 105.6micrometer and a grid depth of 0.279 micrometers was formed.
[0063] The positive type styrene system photoresist 4 corresponding to g line which adjusted the gamma value to 0.7 was applied on the example 5SiC substrate 3, and the occupancy area of a protection-from-light part exposed the resist 4 using the photo mask 1 (less than [Pc=0.50micrometer]) which has the zona-orbicularis-like protection-from-light pattern 2 which decrease in number gradually toward the periphery the part is indicated to be to drawing 5 with 5 times many g line [as this] reduced-projection-exposure machine (drawing 6 (a)).
[0064] Subsequently, the photoresist 4 was developed with the developer (AZ developer by Hoechst A.G.), and the Fresnel lens resist image 5 by which the diameter of 48 micrometers and the configuration with a depth of 3.88 micrometers were reversed was formed (drawing 6 (b)).
[0065] Using parallel monotonous mold reactive-ion-etching equipment, supply the high-frequency power of 250W and on then, CF4 flow-rate 40sccm and the conditions which made the etch rate of a resist 4 quicker than the etch

rate of a substrate 3 Carry out dry etching of the SiC substrate which has the Fresnel lens resist image by which the above-mentioned configuration was reversed, and the Fresnel lens resist image 5 by which the configuration was reversed is compressed and imprinted to the quartz substrate 3 in a lengthwise direction. The Fresnel lens object made from SiC with which the diameter of 48 micrometers and the configuration with a depth of 1.55 micrometers were reversed was formed (drawing 6 (c)).

[0066] After having made into the matrix the Fresnel lens object made from SiC with which the configuration acquired in the example 6 example 5 was reversed, being filled up with the epoxy resin which mixed and obtained Epicoat 152 by the oil-ized shell epoxy company, and the epicure 114 by the oil-ized shell epoxy company between the matrix and the quartz substrate and carrying out heat hardening for four days at 30 degrees C, the matrix was lengthened and removed and the Fresnel lens made of an epoxy resin with a diameter [of 48 micrometers] and a height of 1.55 micrometers was formed.

[0067] The positive type styrene system photoresist 4 corresponding to g line which adjusted the gamma value to 0.7 was applied on the example 7PMMA substrate 3, and the width of face of the protection-from-light part the part (it corresponds to the part of Illustration A) is indicated to be to drawing 7 exposed the resist 4 using the photo mask 1 (less than [Pc=0.50micrometer]) which has the protection-from-light pattern 2 which changes gradually with 5 times many g line [as this] reduced-projection-exposure machine (drawing 8 (a)).

[0068] Subsequently, the photoresist 4 was developed with the developer (AZ developer by Hoechst A.G.), and V ditch type resist image 5 with a slot include angle [of 120 degrees] and a channel depth of 40 micrometers was formed (drawing 8 (b)).

[0069] Using parallel monotonous mold reactive-ion-etching equipment, supply the high-frequency power of 250W and on then, CF4 flow-rate 40sccm and the conditions which made the etch rate of a resist 4 later than the etch rate of a substrate 3 Dry etching of the PMMA substrate which has the above-mentioned V ditch type resist image was carried out, V ditch type resist image 5 was extended and imprinted to the PMMA substrate 3 in the lengthwise direction, and V ditch type made from PMMA with a slot include angle [of 60 degrees] and a channel depth of 120 micrometers was formed (drawing 8 (c)).

[0070] In addition, when the front face of the microstructure formed in the above-mentioned examples 1-7 and a minute press-forming mold was observed by SEM (scanning electron microscope), it saw microscopically and having the shape of smooth surface type was checked.

[0071] Although the desirable example was given above and this invention was explained, this invention is not necessarily limited to the above-mentioned example.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the top view showing the photo mask used in the example of this invention.
[Drawing 2] It is the process explanatory view showing the production process in the example of this invention.
[Drawing 3] It is the top view showing some protection-from-light patterns of the photo mask used in other examples of this invention.
[Drawing 4] It is the process explanatory view showing the production process in other examples of this invention.
[Drawing 5] It is the top view showing some protection-from-light patterns of the photo mask used in other examples of this invention.
[Drawing 6] It is the process explanatory view showing the production process in other examples of this invention.
[Drawing 7] It is the top view showing some protection-from-light patterns of the photo mask used in other examples of this invention.
[Drawing 8] It is the process explanatory view showing the production process in other examples of this invention.
[Description of Notations]
1 Photo Mask
2 Protection-from-Light Pattern
3 Substrate
4 Photoresist
5 Resist Image

[Translation done.]

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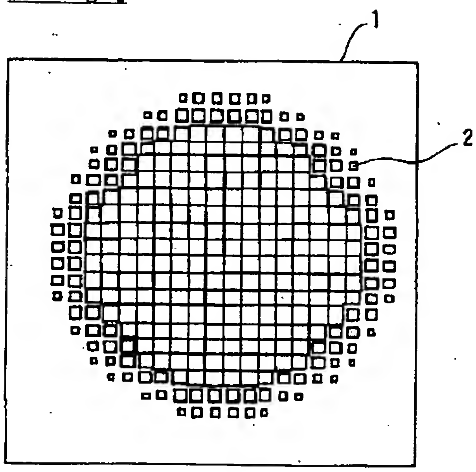
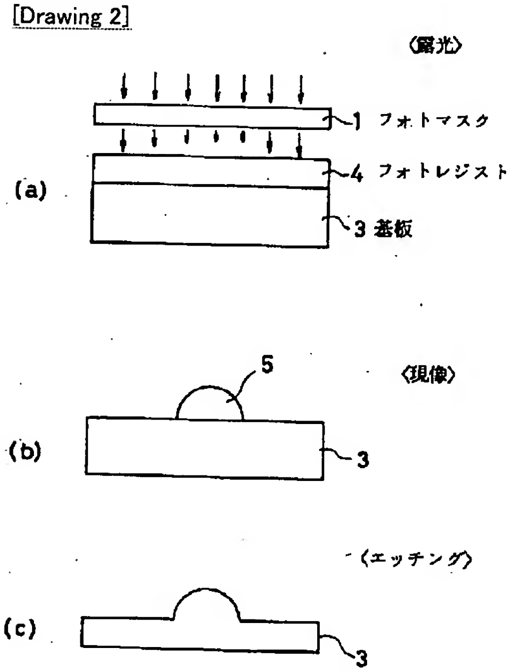
3.In the drawings, any words are not translated.

DRAWINGS

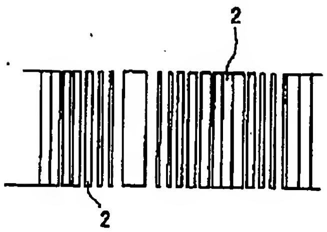
[Drawing 1]



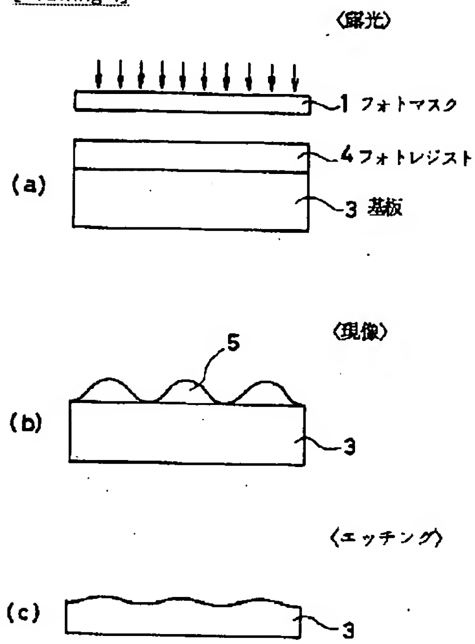
[Drawing 2]



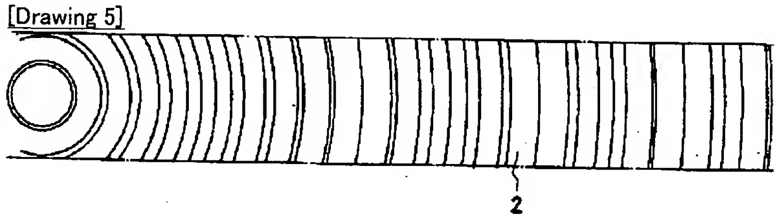
[Drawing 3]



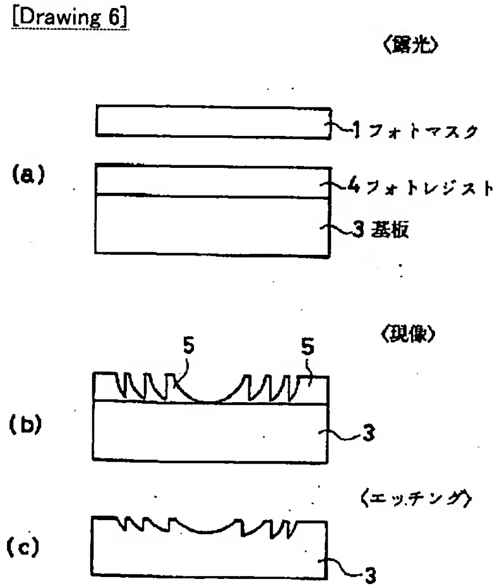
[Drawing 4]



[Drawing 5]

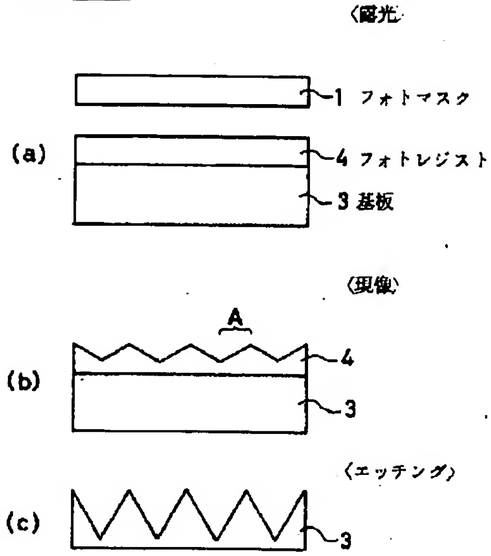


[Drawing 6]



[Drawing 7]

[Drawing 8]



[Translation done.]

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(71)出願人　000113263
ホーヤ株式会社
東京都新宿区中落合２丁目７番５号

(72)発明者　三浦　敏信
東京都新宿区中落合２丁目７番５号　ホーヤ株式会社内

(72)発明者　松本　研二
東京都新宿区中落合２丁目７番５号　ホーヤ株式会社内

(72)発明者　小菅　洋之
東京都新宿区中落合２丁目７番５号　ホーヤ株式会社内

(74)代理人　弁理士　藤村　康夫

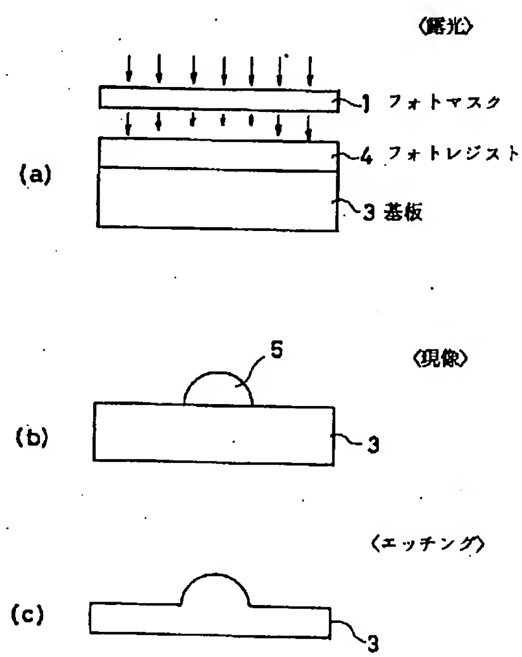
最終頁に続く

(54)【発明の名称】　三次元形状の形成方法、該方法により形成した三次元構造体およびプレス成形型

(57)【要約】

【目的】　微視的に見てなめらかな三次元表面形状の形成方法を提供する。また、微小構造体やプレス成形型を提供する。

【構成】　基板３上にγ値を１．０に調整したレジスト４を塗布し、露光強度を連続的に変化させる特定の遮光パターンを有するマスク１を用いてレジスト４の露光を行う（図２（ａ））。次いで、現像液でレジスト４の現像を行いレジスト像５を形成する（図２（ｂ））。続いて、ドライエッチングにより、レジスト像５を基板３に転写して、三次元表面形状（体）を形成する（図２（ｃ））。



【特許請求の範囲】
【請求項１】　基材上にレジスト層を形成し、該レジスト層に到達する露光強度を連続的に変化させる遮光性パターンを有するリソグラフィー用マスクを用いて、前記レジスト層を露光する工程と、
前記露光後のレジスト層を現像処理して三次元形状のレジスト像を形成する工程と、
前記レジスト像および基材を同時にエッチングしてレジスト像の三次元形状を基材に転写する工程とを有する三次元形状の形成方法において、
レジストの残膜曲線が、緩やかな傾きの残膜曲線となるようなレジストおよび／またはレジスト像形成条件を使用することを特徴とする三次元形状の形成方法。
【請求項２】　前記緩やかな傾きの残膜曲線となるようなレジストが、コントラストが低く低解像力のレジストである請求項１記載の三次元形状の形成方法。
【請求項３】　前記緩やかな傾きの残膜曲線となるようなレジスト像形成条件が、レジストのベーク条件および／または現像条件である請求項１または２記載の三次元形状の形成方法。
【請求項４】　前記緩やかな傾きの残膜曲線となるようなレジストおよび／またはレジスト像形成条件が、レジストのコントラストがガンマ値で２．０以下となるような条件である請求項１ないし３記載の三次元形状の形成方法。
【請求項５】　前記レジスト層を露光する工程において、縮小投影露光を行うことを特徴とする請求項１ないし４記載の三次元形状の形成方法。
【請求項６】　前記現像処理により三次元形状のレジスト像を形成する工程の後に、該三次元形状のレジスト像を該レジストの融点よりも高い温度で加熱することを特徴とする請求項１ないし５記載の三次元形状の形成方法。
【請求項７】　請求項１ないし６記載の三次元形状の形成方法によって製造した微視的に見てなめらかな三次元表面形状を有する三次元構造体。
【請求項８】　請求項１ないし６記載の三次元形状の形成方法によって製造した微視的に見てなめらかな三次元表面形状を有するプレス成形型。
【発明の詳細な説明】
【０００１】
【産業上の利用分野】本発明は、三次元形状の形成方法に関し、特に、マイクロレンズ、マイクロマシーン、マイクロセンサーなどの三次元に精度よく構造制御された微小構造体やこれらの微小構造体を大量生産するためのプレス成形型等の形成方法等に関する。
【０００２】
【従来の技術】近年、半導体製造等に利用されるリソグラフィー技術を用いてマイクロマシーン等の微小構造体の作製が試みられている。具体的には、微小構造形成用基材にフォトレジストを塗布し、フォトマスクを介して露光、現像してレジストパターンを得、エッチングによりこのレジストパターンを微小構造形成用基材に転写して微小構造体を製造する方法が知られているが、この方法だと、得られる微小構造体の深さ方向の形状が矩形に限定されており、深さ方向の形状を制御することができない。
【０００３】そこで、三次元曲面等の三次元に精度よく構造制御された微小構造体の作製方法が各種検討され、提案されている。
【０００４】例えば、矩形に形成した樹脂パターンアレーを加熱熔融して球面形状に変形し、樹脂製凸型マイクロレンズアレーを作製する方法が提案されている（特開平５－４０２１６号公報）（公知例１とする）。
【０００５】また、別の方法として、露光と現像を繰り返して階段状の形状を作製する方法が提案されている（ジャーナル　バキューム　サイエンス　テクノロジー、Ｂ９（６）、１９９１年、３１１７－３１２０頁）（公知例２とする）。
【０００６】さらに、他の方法として、電子ビームの露光量を露光位置により変化させて電子ビームレジストに露光しこれを現像することで電子ビームの露光量に応じた形状を作製する方法が提案されている（特公平２－４４０６０号公報）（公知例３とする）。
【０００７】また、フォトマスクの遮光部分の一部の間隔を露光波長の回折限界以下としこの遮光部分間を透過した光が平面的に連続的に変化する透過光量を与えるフォトマスクを通してフォトレジストを露光し、次いで現像処理することにより、露光された領域に露光量に応じた残像樹脂パターン（三次元形状のレジスト像）を形成する方法が提案されている（アイ　イー　イー　イー　プロシーディングスオン　エム　イー　エム　エス、１９９４年、２０５－２１０頁）（公知例４とする）。
【０００８】一方、微小構造体を大量生産するためのプレス成形型の製造方法に関しては、微細加工の施してある透明母型の形状を感光性樹脂に転写し、その転写した感光性樹脂をエッチングにより下地プレス成型用型に転写する方法が提案されている（特公平６－１５１８４号公報）（公知例５とする）。
【０００９】
【発明が解決しようとする課題】しかしながら、上述した従来の微小構造体の作製方法には、次に示すような問題がある。
【００１０】すなわち、公知例１記載の方法にあっては、熔融した樹脂の表面張力を利用して球面化を行っているため得られる形状が球状のものに限られしまうという問題がある。
【００１１】また、公知例２記載の方法にあっては、レジスト成膜、露光、現像といった工程を複数回繰り返して行う必要があるため製造が煩雑であり、また、フォト

マスクと被露光体との位置合わせを厳密に行う必要があり技術的に製造が難しいという問題がある。

【００１２】さらに、公知例３記載の方法にあっては、すべてのパターンを電子ビームで描画しているので露光に時間がかかり生産性が極めて低いという問題がある。

【００１３】また、公知例４記載の方法にあっては、三次元形状のレジスト像を生産性よく作製できるのであるが、公知例４の方法で実際に作製できる三次元形状のレジスト像は、微視的に見るとその表面形状が階段状（ギザギザ）であるため、なめらかな表面形状が要求されるマイクロレンズ等の製品の製造に実際に応用するのは困難であるという問題がある。

【００１４】さらに、公知例５記載の方法にあっては、母型を機械加工で作製しているため１００μm以下の三次元形状を作製することは困難であるという問題がある。なお、超硬材料を用いたプレス型の作製にあっては、通常砥石による研削、研磨を行うため、被加工型の大きさがミリメートル以上に制限されるという問題もある。

【００１５】本発明は上述した問題点にかんがみてなされたものであり、微視的になめらかな三次元表面形状の形成方法の提供を目的とする。また、微視的になめらかな三次元表面形状を有する三次元に精度よく構造制御された微小構造体やこれらの微小構造体を大量生産するためのプレス成形型等の提供を目的とする。

【００１６】

【課題を解決するための手段】上記目的を達成するために本発明の三次元形状の形成方法は、基材上にレジスト層を形成し、該レジスト層に到達する露光強度を連続的に変化させる遮光性パターンを有するリソグラフィー用マスクを用いて、前記レジスト層を露光する工程と、前記露光後のレジスト層を現像処理して三次元形状のレジスト像を形成する工程と、前記レジスト像および基材を同時にエッチングしてレジスト像の三次元形状を基材に転写する工程とを有する三次元形状の形成方法において、レジストの残膜曲線が、緩やかな傾きの残膜曲線となるようなレジストおよび／またはレジスト像形成条件を使用する構成としてある。

【００１７】また、本発明の三次元形状の形成方法は、上記本発明の三次元形状の形成方法において、前記緩やかな傾きの残膜曲線となるようなレジストが、コントラストが低く低解像力のレジストである構成、前記緩やかな傾きの残膜曲線となるようなレジスト像形成条件が、レジストのベーク条件および／または現像条件である構成、前記緩やかな傾きの残膜曲線となるようなレジストおよび／またはレジスト像形成条件が、レジストのコントラストがガンマ値で２．０以下となるような条件である構成、前記レジスト層を露光する工程において、縮小投影露光を行う構成、あるいは、　前記現像処理により三次元形状のレジスト像を形成する工程の後に、該三次元形状のレジスト像を該レジストの融点よりも高い温度で加熱する構成、としてある。

【００１８】また、本発明の微小三次元構造体は、上記三次元形状の形成方法によって、微視的に見てなめらかな三次元表面形状を有する三次元構造体を製造する構成としてある。

【００１９】さらに、本発明のプレス成形型は、上記三次元形状の形成方法によって、微視的に見てなめらかな三次元表面形状を有するプレス成形型を製造する構成としてある。

【００２０】以下、本発明を詳細に説明する。本発明の三次元形状の形成方法においては、まず、基材上にレジスト層を形成し、このレジスト層に到達する露光強度を連続的に変化させる遮光性パターンを有するリソグラフィー用マスクを用いて、前記レジスト層を露光する。

【００２１】ここで、基材材料としては、耐光性や機械的強度の高い材料であればいかなる材料でも使用することができ特に制限されないが、例えば、ＳｉＣ、WC、ＴｉＣ、Cr_3C_2、ＴｉＮ、Al_2O_3等の超硬材料、石英等のガラス材料、Ｓｉ、Ｇｅ等の赤外線透過材料、ポリアミド類などに代表されるエンジニアリングプラスチック等が挙げられる。基材の形状は特に制限されないが、通常基板が用いられる。

【００２２】また、レジスト層の形成は、溶液タイプのレジストについてはスピンコート、ディップコート、スプレーコート等の既存の方法により形成し、無機レジスト等の固形タイプレジストについては真空蒸着、スパッタリング、ＣＶＤ等の既存の方法により形成する。

【００２３】本発明では、レジスト層に到達する露光強度を連続的に変化させる遮光性パターンを有するリソグラフィー用マスクを用いる。これは、一般にレジストの現像後の残膜厚はレジスト上に露光された露光光強度（露光量）に対応して変化するため、レジスト層に到達する露光強度を連続的に変化させてレジストの現像後の残膜厚を連続的に変化させるためである。

【００２４】ここで、レジスト層に到達する露光強度を連続的に変化させる遮光性パターンを有するリソグラフィー用マスクとしては、いくつかの種類が挙げられる。例えば、遮光部分の光学濃度の少なくとも一部を連続的に変化させたマスクが挙げられる。このようなマスクは、遮光膜の厚みを連続的に変化させるか、あるいは遮光膜の組成を連続的に変化させて得られる。

【００２５】他のマスクとしては、マスクの遮光部分の間隔の少なくとも一部を露光波長の回折限界以下の間隔としたマスク、あるいはマスクの開口部分の間隔の少なくとも一部を露光波長の回折限界以下の間隔としたマスクが挙げられる。この場合、マスクの遮光部分の間隔あるいは開口部分の間隔を露光波長の回折限界以下の間隔とするには、これらの間隔を下記に示す限界ピッチ以下とすればよい。

$Pc=\lambda/NA(1+\sigma)$

ここで、Pcは限界ピッチ、λは露光波長、ＮＡは露光機の開口数、σはピクセル内の遮光部分の充填率をそれぞれ示す。ここで遮光部分の充填率に関し、遮光部分の形状は一つのピクセル内の遮光面積が可変できる形状であれば特に制限されないが、線状、ドット状、矩形状などの形状が主として用いられる。

【００２６】なお、ステッパーを用いて縮小露光する場合にあっては、実際のマスク（レチクル）の遮光部分の間隔あるいは開口部分の間隔を露光波長の回折限界以下の間隔とするのではなく、縮小投影されたレジスト上における遮光部分の間隔あるいは開口部分の間隔が露光波長の回折限界以下の間隔となるようにする。

【００２７】上述したマスクは、回折の影響を受けることなく正確に転写できるパターンの幅（ピッチ）あるいはパターンの面積を１としこの場合の露光強度を１とした場合、パターンの幅あるいは面積を１以下とし回折の影響を利用して１以下の中間的な露光強度を得ようとするものである。

【００２８】さらに他のマスクとしては、マスクの遮光部分の間隔の少なくとも一部をレジストの解像限界以下の間隔としたマスク、あるいはマスクの開口部分の間隔の少なくとも一部をレジストの解像限界以下の間隔としたマスクが挙げられる。例えば、レジストの解像限界が１μmであれば、マスクの遮光部分の間隔あるいは開口部分の間隔を１μm以下の間隔とする。これは、レジストの解像限界（解像力）が異なれば上述した限界ピッチも異なるためこれを考慮しようとするものである。したがって、レジストの解像限界が２μmであれば、マスクの遮光部分の間隔あるいは開口部分の間隔を２μm以下の間隔とする。

【００２９】なお、上述した露光強度を連続的に変化させる遮光性パターンを有するリソグラフィー用マスクの形成材料に関しては、マスク基板としては露光波長に対して透明な材料であれば全て使用が可能であり、遮光部を構成する遮光膜としてはマスクを通して被転写体に必要とされる光学濃度のコントラストを有するパターンを転写できる物質であれば全て使用が可能である。具体的には、マスク基板としては、例えば、石英ガラス板、アルミノボロシリケートガラス板などが挙げられる。また、遮光膜材料としては、例えば、クロム、酸化クロム、タングステンシリサイド、タンタルシリサイド、モリブデンシリサイド、銀コロイドなどが挙げられる。

【００３０】上記リソグラフィー用マスクには、フォトマスク、Ｘ線マスクの他、電子線マスクやイオンビームマスクも含まれる。また、露光方法には、密着露光（コンタクト露光）、近接露光（プロキシミティ露光）、等倍投影露光（ミラープロジェクション露光）等の等倍露光や、縮小投影露光などが含まれる。縮小投影露光を用いると等倍露光に比べより微細な微小構造体を容易に形成できる。さらに、露光光源には、紫外・可視光、エキシマレーザ、Ｘ線（シンクロトロン放射光含む）、、電子線、イオンビームなどが含まれる。

【００３１】本発明においては、上記露光後のレジスト層を現像処理して三次元形状のレジスト像を形成する際に、微視的に見てなめらかな表面を有するレジスト像が形成される条件を使用することを特徴とする。これは、コントラストが高く高解像力のレジストを使用すると、上記特定の遮光性パターンを有するリソグラフィー用マスクによってレジスト層に到達する露光強度が連続的に変化しているといっても、この露光強度の連続的変化は微視的に見ると階段状となっているため、得られる三次元形状のレジスト像の表面が微視的に見て階段状（ギザギザ）となってしまうからである。

【００３２】そこで、本発明者らは、シャープなレジスト像が形成できないような条件を積極的に使用することを考えついた。具体的には、本発明では、緩やかな傾きの残膜曲線となるようなレジストおよび／またはレジスト像形成条件を使用する。

【００３３】ここで、レジストの残膜曲線（特性曲線）は、一般には横軸に照射量の常用対数をとり縦軸に現像後の膜厚を塗布膜厚で規格化した値（残膜率）をとって得られる曲線であり、この残膜曲線の形状（傾き等）は、レジスト自身の特性（レジストを構成する樹脂の種類等）や、レジストの熱処理条件（プリベーク条件等）、現像処理条件、露光光源等によって変化する。また、残膜曲線の傾きはガンマ値（γ値）と呼ばれ、このγ値は、レジストのコントラストを表す指標となり、この値が高いほどコントラストは上がり解像度も上がる。一般的にネガ型レジストのγ値は残膜率が０．５となるときの残膜曲線の傾き（傾き角の正接値）で定義され、ポジ型レジストのγ値は残膜率が０となるときの残膜曲線の傾きで定義される。

【００３４】したがって、全体として緩やかな傾きの残膜曲線となるようなレジストおよびレジスト像形成条件を使用すると、コントラストが低く低解像力のなめらかな形状（エッジ等）のレジスト像が形成できる。これは、残膜曲線の傾きが緩やかであると、露光強度の広い範囲でレジストの残膜厚を制御でき、露光強度の微妙な変化に応じたレジスト残膜厚を得ることができるからである。

【００３５】ここで、緩やかな傾きの残膜曲線となるようなレジストとしては、コントラストが低く低解像力のレジストが挙げられるが、このようなレジストは、レジストを構成する樹脂の種類や、増感材、溶剤等の含有量などを選択調整して調製する。

【００３６】また、緩やかな傾きの残膜曲線となるようなレジスト像形成条件としては、レジストのベーク条件および／または現像条件が挙げられる。これは、上述したように残膜曲線の形状がレジストの熱処理条件や現像

処理条件によって変化するためである。

【００３７】現像条件としては、現像時間、現像方法、現像液の種類、濃度および温度、レジストの溶解特性などが挙げられ、緩やかな傾きの残膜曲線となるようにこれらの条件を設定する。特に、現像時間やレジストの溶解特性は現像後のレジスト形状（レジストプロフィル）に影響を与えるためこれを考慮して条件を設定する。具体的には、これらの条件を種々変化させて残膜曲線を実際に作成しこれに基づき各種条件を設定すればよいまた、現像温度や現像方法（スプレー法におけるスプレー圧あるいはディッピング法における現像液の対流速度等）なども解像力に影響を与えるためこれらを考慮して条件を設定する。

【００３８】プリベークは通常レジスト膜中から溶剤を除去する目的で行われるが、本発明では、緩やかな傾きの残膜曲線となるように、プリベーク温度およびプリベーク時間を設定する。

【００３９】なお、通常の半導体プロセスではガンマ値が２．０以上の高コントラスト、高解像度のレジストが使用されていることを考慮すると、緩やかな傾きの残膜曲線となるようなレジストおよび／またはレジスト像形成条件としては、レジストのコントラストがガンマ値で２．０以下となるような条件であるといえる。ここで、γ値の値は、上述した残膜曲線の場合と同様に、レジスト自身の特性や、レジストの熱処理条件、現像処理条件等によって変化するので、これらを調整すれば所望のγ値を得ることができる。γ値の値は、上記の理由から２．０以下であることが好ましいのであるが、本発明の効果をより確かなものにするためにはγ値が１．５以下であることが好ましく、１．０以下であることがさらに好ましい。γ値の下限に関しては、露光強度の微妙な変化に応じたレジスト残膜厚が得られるようにするため、極端に低くならないように注意すればよい。

【００４０】なお、レジストを構成する樹脂の種類としては、例えば、シンナメート系の光二量化型感光性樹脂、金属イオン重クロム酸型感光性樹脂などの光架橋性樹脂、アジド系の光分解架橋型感光性樹脂、ジアゾ系の光分解不溶型感光性樹脂、キノンジアジド系の光分解可溶型感光性樹脂などの光分解性樹脂、不飽和ポリエステル系感光性樹脂、アクリレート系感光性樹脂、ナイロン系感光性樹脂、カチオン重合系感光性樹脂などの光重合性樹脂や、カルコゲナイド系の無機レジスト等が挙げられる。これらの樹脂は単独で使用してもよく、二種類以上を混合して使用してもよい。

【００４１】本発明では、上記現像処理により三次元形状のレジスト像を形成する工程の後に、三次元形状のレジスト像をレジストの融点よりも高い温度で加熱してもよい。これによりレジストが変形してなめらかとなる。このように上記工程の後に加熱熔融を行うと、単独で加熱熔融する場合に比べ、うねりが少なく局部的な欠陥が少なく、かつ、よりなめらかな三次元形状のレジスト像が短時間で得られる。

【００４２】本発明では、上記現像工程の後、レジスト像および基材を同時にエッチングしてレジスト像の三次元形状を基材に転写する。この場合、レジスト像と同一の形状を転写するにはレジストと下地基材のエッチング速度を等しくする。また、縦方向に圧縮した形状を得るにはレジストのエッチング速度を下地基材のエッチング速度より速くし、逆に縦方向に引き延ばした形状を得るにはレジストのエッチング速度を下地基材のエッチング速度より遅くする。

【００４３】なお、エッチング速度は使用するレジストとエッチング装置におけるエッチング条件によって変化するので、これらを総合的に判断してエッチング条件を選択する必要がある。特に、ドライエッチング装置を使用する場合には、装置の構造（種類）やエッチング圧力（ガス圧）、エッチング出力、ガス流量、基板温度などの条件によってエッチング速度が変化するので、これらを総合的に判断してエッチング条件を選択する必要がある。

【００４４】なお、エッチング方法としてはウエットエッチングおよびドライエッチングが挙げられるが、レジストパターンの形状を極力正確に基板に転写するためには、ドライエッチングを採用することが好ましい。ドライエッチング装置は、特に制限されないが、例えば、平行平板型リアクティブイオンエッチング装置やマグネトロンイオンエッチング装置等の公知のドライエッチング装置が使用される。

【００４５】ドライエッチングに使用するガスとしては、CF_4、CHF_3、C_2F_6、Cl_2に代表されるようなフッ素系、塩素系の単体ガス、またはこれらのガスを含む混合ガス等が好ましい。また、これらのガスに、酸素もしくは水素などのガス、あるいはＨｅ、Ａｒなどの不活性ガスを、必要に応じ混合してもよい。

【００４６】上記本発明方法によれば、微視的に見てなめらかな三次元表面形状の形成できる。また、本発明方法によれば、三次元に精度よく構造制御されたなめらかな表面の微小構造体を効率よく製造でき、特に、実用上微視的になめらかな表面形状を必要とする微小光学部品の製造方法として特に有効である。さらに、本発明方法によれば、従来得ることのできなかった三次元に精度よく構造制御されたなめらかな表面の微小プレス成形型を効率よく製造できる。なお、本発明の三次元形状の形成方法は、微小構造体に限られず、通常の大きさの構造体にも適用できる。

【００４７】本発明の他の発明は、上述した三次元形状の形成方法によって製造したことを特徴とする三次元構造体である。本発明の三次元構造体は、微視的になめらかな三次元表面形状を有する三次元に精度よく構造制御された微小構造体であり、実用上微視的になめらかな表

面形状を必要とする微小光学部品として特に有効である。すなわち、本発明は、従来、実用製品として得ることのできなかった微小光学部品の実用化を図ったものであり産業上の利用価値が極めて高い。

【００４８】なお、微小構造体の用途や種類は特に制限されない。微小構造体の用途としては、例えば、微小光学部品、マイクロマシーン部品、マイクロセンサー部品としての用途が挙げられる。また、微小光学部品の種類としては、凸型レンズ、凹型レンズ、アナモフィックレンズ、レンチキュラーレンズ等の球面レンズや非球面レンズ、三角波形グレーティング、正弦波形グレーティング、台形波形グレーティング等のグレーティング、プリズム、ゾーンプレート、フレネルレンズ、ホログラフィックレンズなどが挙げられる。マイクロマシーン部品やマイクロセンサー部品の種類としては、凸型球面体、凹型球面体、非球面体、錐状突起体などが挙げられる。

【００４９】なお、本発明では、複数の微小構造体を任意の配置で配置して作製することができ、さらに、微小構造体を連続して作製したり、連続一体型の微小構造連続体を作製することができる。

【００５０】本発明の他の発明は、上述した三次元形状の形成方法によって製造したことを特徴とするプレス成形型である。本発明のプレス成形型によれば、微小構造体を容易に大量生産できる。

【００５１】ここで、微小プレス成形型に加工される基材としては、耐光性や耐熱性、機械的強度の高い材料であればいかなる材料でも使用することができ特に制限されないが、例えば、ＳｉＣ、WC、ＴｉＣ、Cr_3C_2、ＴｉＮ、Al_2O_3等の超硬材料、石英等のガラス材料、Ｓｉ、Ｇｅ等の赤外線透過材料、ポリアミド類などに代表されるエンジニアリングプラスチック等が挙げられる。

【００５２】なお、プレスする材料としてはガラスやプラスチック等が用いられる。この場合、ガラスとしてはＢＫ－７等の光学ガラスが用いられる。また、プレスする材料としてプラスチックを用いる場合には、プレス型に石英等の透明材料を用い、紫外線硬化樹脂をプレス型と被転写基板との間に充填し、紫外線を照射して樹脂を硬化させて樹脂製の微小光学素子等をプレス成型できる。ここで、紫外線硬化樹脂としては、ポリスチレン樹脂、エポキシ樹脂、ウレタン樹脂、ポリオレフィン樹脂、ポリイミド樹脂、ポリアミド樹脂、ポリエステル樹脂、あるいはこれらの樹脂の混合物等公知の樹脂が使用できる。

【００５３】さらに、プレス型に耐熱性材料を用い、熱硬化樹脂をプレス型と被転写基板との間に充填し、加熱によって熱硬化樹脂を硬化させて樹脂製の微小光学素子等を成型することもできる。ここで、熱硬化樹脂としては、ポリスチレン樹脂、アクリル樹脂、エポキシ樹脂、ウレタン樹脂、ポリオレフィン樹脂、ポリイミド樹脂、ポリアミド樹脂、ポリエステル樹脂、あるいはこれらの樹脂の混合物等公知の樹脂が使用できる。

【００５４】

【実施例】以下、実施例にもとづき本発明をさらに具体的に説明する。

【００５５】実施例１

石英基板３上にγ値を１．０に調整したｇ線対応ポジ型スチレン系フォトレジスト４を塗布し、図１に示すような円形遮光パターン２を有するフォトマスク１を用いて、等倍ｇ線密着露光機でレジスト４の露光を行った（図２（ａ））。ここで、図１に示すフォトマスク１は、円外周に向かって遮光部分の占有面積が徐々に減少する遮光パターン２を有するものとし、遮光部分の間隔が限界ピッチ（Pc＝０．１１μｍ）以下としたものを使用した。

【００５６】次いで、現像液（ヘキスト社製ＡＺデベロッパー）でフォトレジスト４の現像を行い（現像時間１２０秒、プリベーク温度９０℃、時間６０分）、対角２０μｍ、高さ１μｍの凸型球面レジスト像５を形成した（図２（ｂ））。

【００５７】続いて、平行平板型リアクティブイオンエッチング装置を用い、２５０Wの高周波電力を供給し、C_2F_6流量５０ｓｃｃｍ、レジスト４のエッチング速度を基板３のエッチング速度と同一とした条件で、上記凸型球面レジスト像を有する石英基板をドライエッチングし、凸型球面レジスト像５を石英基板３に転写して、対角２０μｍ、高さ１μｍの石英製凸型球面体を形成した（図２（ｃ））。

【００５８】実施例２

実施例１で得られた対角２０μｍ、高さ１μｍの石英製凸型球面体を母型とし、光重合性モノマー（日本化学薬社製２Ｐ用モノマーＩＮＣ３１２）を母型と基板との間に充填し、２０mW／cm^2の照射強度で、２４０秒間水銀灯を照射しモノマーを重合硬化して、対角２０μｍ、深さ１μｍの樹脂製凹型球面体を形成した。

【００５９】実施例３

ＳｉＣ基板３上にγ値が２．０であるｇ線対応ポジ型スチレン系フォトレジスト４を塗布し、図３にその一部が示されている遮光部分の間隔が徐々に変化する遮光パターン２を有するフォトマスク１（Pc＝０．１１μｍ以下）を用いて、等倍ｇ線密着露光機でレジスト４の露光を行った（図４（ａ））。

【００６０】次いで、現像液（ヘキスト社製ＡＺデベロッパー）でフォトレジスト４の現像を行い、さらに、２００℃で３０分間熱処理を施して、格子ピッチ１０５．６μｍ、格子深さ０．６９８μｍの正弦波回折格子レジスト像５を形成した（図４（ｂ））。

【００６１】続いて、平行平板型リアクティブイオンエッチング装置を用い、２５０Wの高周波電力を供給し、CF_4流量４０ｓｃｃｍ、レジスト４のエッチング速度

を基板３のエッチング速度より速くした条件で、上記正弦波回折格子レジスト像を有するＳｉＣ基板をドライエッチングし、正弦波回折格子レジスト像５を石英基板３に縦方向に圧縮して転写して、格子ピッチ１０５．６μｍ、格子深さ０．２７９μｍの正弦波回折格子を形成した（図４（ｃ））。

【００６２】実施例４
実施例３で得られた格子ピッチ１０５．６μｍ、格子深さ０．２７９μｍの正弦波回折格子を母型とし、二酸化ケイ素７０重量％、酸化鉛２５重量％、その他数種類の微量元素成分からなるガラスを加熱後にプレスして、格子ピッチ１０５．６μｍ、格子深さ０．２７９μｍのガラス製正弦波回折格子を形成した。

【００６３】実施例５
ＳｉＣ基板３上にγ値を０．７に調整したｇ線対応ポジ型スチレン系フォトレジスト４を塗布し、図５にその一部が示されている外周に向かって遮光部分の占有面積が徐々に減少する輪帯状遮光パターン２を有するフォトマスク１（Pc＝０．５０μｍ以下）を用いて、ｇ線５倍縮小投影露光機でレジスト４の露光を行った（図６（ａ））。

【００６４】次いで、現像液（ヘキスト社製ＡＺデベロッパー）でフォトレジスト４の現像を行い、直径４８μｍ、深さ３．８８μｍの形状が反転されたフレネルレンズレジスト像５を形成した（図６（ｂ））。

【００６５】続いて、平行平板型リアクティブイオンエッチング装置を用い、２５０Ｗの高周波電力を供給し、ＣＦ4流量４０ｓｃｃｍ、レジスト４のエッチング速度を基板３のエッチング速度より速くした条件で、上記形状が反転されたフレネルレンズレジスト像を有するＳｉＣ基板をドライエッチングし、形状が反転されたフレネルレンズレジスト像５を石英基板３に縦方向に圧縮して転写して、直径４８μｍ、深さ１．５５μｍの形状が反転されたＳｉＣ製フレネルレンズ体を形成した（図６（ｃ））。

【００６６】実施例６
実施例５で得られた形状が反転されたＳｉＣ製フレネルレンズ体を母型とし、油化シェルエポキシ社製エピコート１５２と油化シェルエポキシ社製エピキュア１１４とを混合して得たエポキシ樹脂を母型と石英基板との間に充填し、３０℃で４日間加熱硬化させた後、母型を引き剥して、直径４８μｍ、高さ１．５５μｍのエポキシ樹脂製フレネルレンズを形成した。

【００６７】実施例７
ＰＭＭＡ基板３上にγ値を０．７に調整したｇ線対応ポジ型スチレン系フォトレジスト４を塗布し、図７にその一部（図示Ａの部分に対応する）が示されている遮光部分の幅が徐々に変化する遮光パターン２を有するフォトマスク１（Pc＝０．５０μｍ以下）を用いて、ｇ線５倍縮小投影露光機でレジスト４の露光を行った（図８（ａ））。

【００６８】次いで、現像液（ヘキスト社製ＡＺデベロッパー）でフォトレジスト４の現像を行い、溝角度１２０°、溝深さ４０μｍのＶ溝型レジスト像５を形成した（図８（ｂ））。

【００６９】続いて、平行平板型リアクティブイオンエッチング装置を用い、２５０Ｗの高周波電力を供給し、ＣＦ4流量４０ｓｃｃｍ、レジスト４のエッチング速度を基板３のエッチング速度より遅くした条件で、上記Ｖ溝型レジスト像を有するＰＭＭＡ基板をドライエッチングし、Ｖ溝型レジスト像５をＰＭＭＡ基板３に縦方向に引き延ばして転写して、溝角度６０°、溝深さ１２０μｍのＰＭＭＡ製Ｖ溝型を形成した（図８（ｃ））。

【００７０】なお、上記実施例１～７で形成した微小構造体および微小プレス成形型の表面をＳＥＭ（走査型電子顕微鏡）で観察したところ微視的に見てなめらかな表面形状であることが確認された。

【００７１】以上好ましい実施例をあげて本発明を説明したが、本発明は必ずしも上記実施例に限定されるものではない。

【００７２】
【発明の効果】以上説明したように本発明の三次元表面形状の形成方法によれば、微視的に見てなめらかな三次元表面形状を形成できる。また、本発明方法によれば、三次元に精度よく構造制御されたなめらかな表面の微小構造体を効率よく製造でき、特に、実用上微視的になめらかな表面形状を必要とする微小光学部品の製造方法として特に有効である。さらに、本発明方法によれば、従来得ることのできなかった三次元に精度よく構造制御されたなめらかな表面の微小プレス成形型を効率よく製造できる。

【００７３】また、本発明の微視的に見てなめらかな三次元表面形状を有する微小三次元構造体は、従来実用製品として得ることのできなかった微小光学部品の実用化を図ったものであり産業上の利用価値が極めて高い。

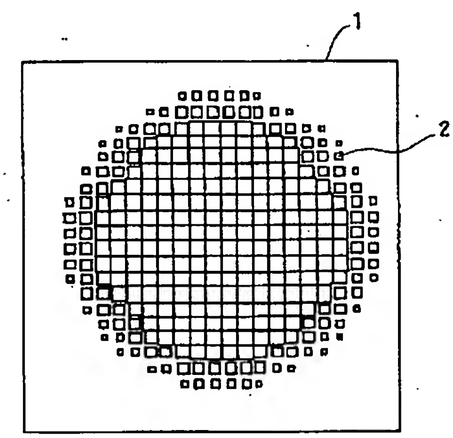
【００７４】さらに、本発明のプレス成形型によれば、微小構造体を容易に大量生産できる。

【図面の簡単な説明】
【図１】　本発明の実施例で使用したフォトマスクを示す平面図である。
【図２】　本発明の実施例における製造工程を示す工程説明図である。
【図３】　本発明の他の実施例で使用したフォトマスクの遮光パターンの一部を示す平面図である。
【図４】　本発明の他の実施例における製造工程を示す工程説明図である。
【図５】　本発明の他の実施例で使用したフォトマスクの遮光パターンの一部を示す平面図である。
【図６】　本発明の他の実施例における製造工程を示す工程説明図である。

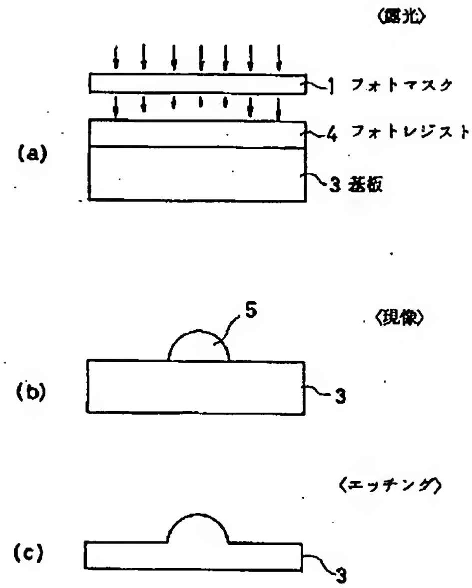
【図７】　本発明の他の実施例で使用したフォトマスクの遮光パターンの一部を示す平面図である。
【図８】　本発明の他の実施例における製造工程を示す工程説明図である。
【符号の説明】

1　フォトマスク
2　遮光パターン
3　基板
4　フォトレジスト
5　レジスト像

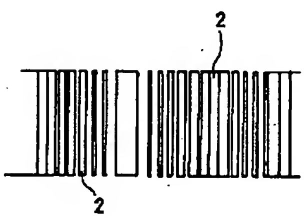
【図１】



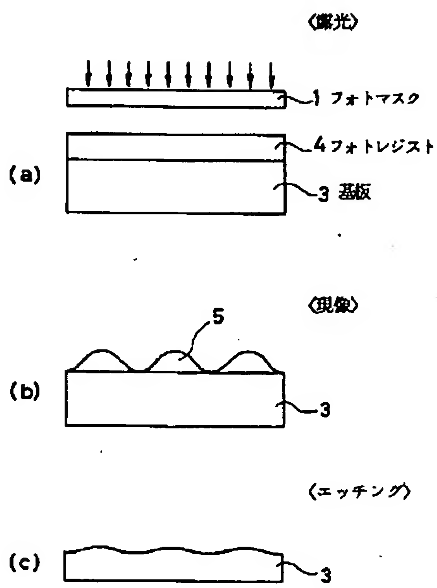
【図２】



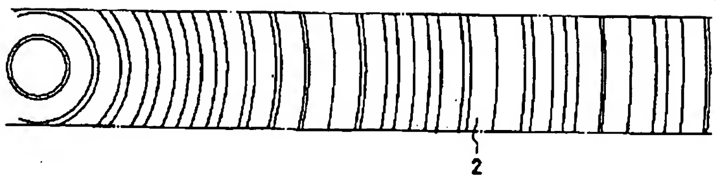
【図３】



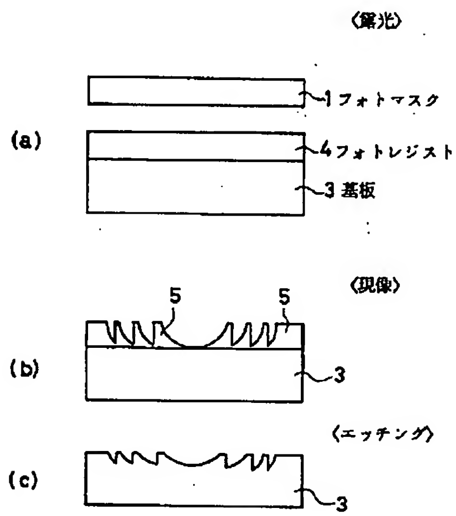
【図４】



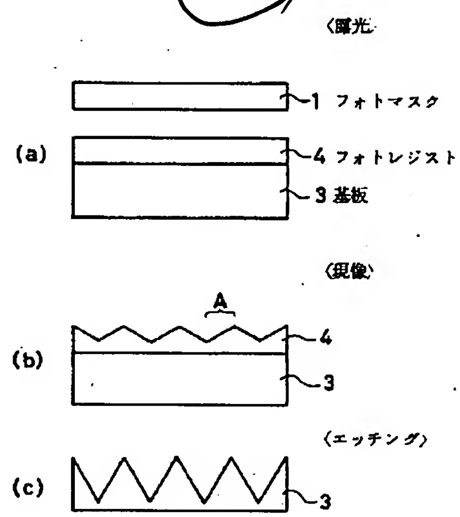
【図５】



【図６】



【図８】



【図７】

フロントページの続き

(72)発明者　山口　洋一
東京都新宿区中落合２丁目７番５号　ホーヤ株式会社内